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ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY

VOLUME 4 - FORMALDEHYDE MANUFACTURE WITH THE SILVER CATALYST PROCESS

AIR PRODUCTS AND CHEMICALS, INCORPORATED

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

MARCH 1975

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ENGINEERING AND COST STUDY OF AIR POLLUTION CONTROL FOR THE PETROCHEMICAL INDUSTRY VOLUME 4: FORMALDEHYDE MANUFACTURE WITH THE SILVER CATALYST PROCESS

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This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by twelve distinctly different processes has been selected for this type of in-depth study. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c, and d).

This volume covers the manufacture of formaldehyde with the silver catalyst process. Included is a process and industry description, an engineering description of available emission control systems, the cost of these systems, and the financial impact of emission control on the industry. Also presented are suggested air episode procedures and plant inspection procedures.

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by

R. B. Morris, F. B. Higgins, Jr.,
J. A. Lee, R. Newirth, and J. W. Pervier

Houdry Division
Air Products and Chemicals, Inc.
P. O. Box 427
Marcus Hook, Pennsylvania 19061

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PETROCHEMICAL AIR POLLUTION STUDY

INTRODUCTION TO SERIES

This document is one of a series prepared for the Environmental Protection Agency (EPA) to assist it in determining those petrochemical processes for which standards should be promulgated. A total of nine petrochemicals produced by 12 distinctly different processes has been selected for this type of in-depth study. These processes are considered to be ones which might warrant standards as a result of their impact on air quality. Ten volumes, entitled Engineering and Cost Study of Air Pollution Control for the Petrochemical Industry (EPA-450/3-73-006a through j) have been prepared.

A combination of expert knowledge and an industry survey was used to select these processes. The industry survey has been published separately in a series of four volumes entitled Survey Reports on Atmospheric Emissions from the Petrochemical Industry (EPA-450/3-73-005a, b, c and d).

The ten volumes of this series report on carbon black, acrylonitrile, ethylene dichloride, phthalic anhydride (two processes in a single volume), formaldehyde (two processes in two volumes), ethylene oxide (two processes in a single volume) high density polyethylene, polyvinyl chloride and vinyl chloride monomer.

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The study reported in this volume, by its nature, relied on the fullest cooperation of the companies engaged in the production of formaldehyde. Had their inputs been withheld, or valueless, the study would not have been possible or at least not as extensive as here reported. Hence, Air Products wishes to acknowledge this cooperation by listing the contributing companies.

Allied Chemical Corporation
Borden Chemical Company
Celanese Corporation
E. I. duPont deNemours & Company
GAF Corporation
Georgia Pacific Corporation
Gulf Oil Corporation
Hercules, Inc.
Hooker Chemical Company
Monsanto Company
Reichhold Chemical Company
Tenneco Chemical Company
Wright Chemical Company

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SUMMARY

The formaldehyde industry has been studied to determine the extent of air pollution resulting from the operations of the various plants and processes of the industry. The purpose of the work was to provide the Environmental Protection Agency with a portion of the basic data required in order to reach a decision on the need to promulgate air emission standards for the industry.

It was concluded that there are two basic processes for the production of formaldehyde. They both utilize methanol as a raw material in an air oxidation process. Neither appears to have any significant advantage which would alter its relative growth rate. A third process, utilizing partial oxidation of light hydrocarbons to produce formaldehyde appears to be obsolete. The principal differences between the two methanol based processes are the catalyst and the methanol/air ratio. The subject of this report is the process utilizing a silver catalyst and a methanol rich feed mixture with air. A separate study devotes itself to the other process which uses a mixed metal oxide catalyst and a methanol lean feed mixture with air. (Report Number EPA-450/3-73-006e.)

In general terms, the air emissions from the silver catalyst process fall into the categories of hydrocarbons (formaldehyde, methanol, methyl formate and methylal) and carbon monoxide. As practiced today, virtually no oxides of nitrogen, oxides of sulfur or particulates are emitted from the process. Additionally, although not considered a pollutant, significant quantities of hydrogen are emitted. This fact contributes to the current trend to burn the waste stream, which could in turn, contribute to an increase in the emissions of nitrogen oxide in the waste gas incineration process. The emission factor for the process is about 0.022 lbs./lb. of 37% formaldehyde. Of this total, over 80 percent is carbon monoxide which in 1973 was equivalent to over 100 million lbs. of CO emitted into the atmosphere. The hydrocarbon emissions were nearly 25 million lbs. during 1973 and although there is considerable variation from plant to plant, the best generalization is that the total is about 75 percent methanol, 25 percent formaldehyde with only traces of other hydrocarbons. It has been estimated that emissions in 1985 will increase to about 225 million lbs./year of carbon monoxide plus about 50 million lbs./year of hydrocarbons, if all future silver process plants are built as is typical today.

Formaldehyde is normally marketed as a 37-51 percent water solution. Therefore, all plants have a water scrubber (absorber) on the main process stream before it is vented to the atmosphere. Most plants also have a mist eliminator on this stream to minimze the entrainment of water from the absorber. In addition, four of the plants surveyed have an incineration device on the waste stream. Two of these use the waste gas as a supplement to their steam boiler fuel and the other two incinerate the waste gas without energy recovery. All four believe that combustion of carbon monoxide and hydrocarbons is nearly complete and that nitrogen oxide generation is practically nil. This belief is probably valid but no analytical data exist to support it. If all plants were equipped with efficient incineration devices, the 1985 emissions of carbon monoxide from the process would drop to nearly zero and the hydrocarbon emissions would drop to about ten million lbs./year. The explanation of this fact is that because of the methanol rich feed stream a considerable quantity of methanol passes through the reactor unconverted. It is then recovered by fractionation and recycled. Vent losses from the fractionation amount to about 25 percent of the hydrocarbon emissions from the process. The mixed oxide process does not

SUMMARY (continued)

require a comparable fractionation step because of the methanol lean feed. Only one respondent to the questionnaire reported pollution control on the fractionator vent in the form of a water scrubber, although it is believed that at least one plant recycles some portion of the vent. The study proposes a "total recycle" type of system which reduces fractionator vent emissions to zero. However, due to the fact that it may result in a build up of minor impurities, it cannot be considered as the ultimate solution to the problem although a continuously purged modification of the concept may be workable.

In summary, the study has concluded that the most feasible air pollution control system for new plants using the silver catalyst process consists of utilizing the waste gas as a fuel supplement in the boiler house and effecting a total (or partical) recycle of vent gases from the product fractionator. This would result in practically no increase in today's level of emissions if all new silver process formaldehyde plants incorporated this system. In addition, a fuel gas saving of about three billion standard cubic feet per year of natural gas would be realized by 1985. The estimated capital cost of installing this equipment on all new plants is less than $50,000 per plant (1973 dollars) or about $3,000,000 for the industry by 1985. Neither aspect of this "most feasible" pollution control system may be applicable to existing plants but pollution reductions have been demonstrated by means of incinerators on absorber vent gases and by a scrubber on the fractionator vent. The cost of these devices on all existing plants has been estimated to be less than $3,000,000 (1973 dollars) but because of unknown problems in individual plants, the estimate may not be valid in all cases.

From the foregoing, it appears that the major efforts for industry research should be in catalyst research to improve yields and perhaps in the use of oxygen enriched feeds to make the waste gas more readily combustible (or recyclable) through nitrogen content reduction. A study on the recycling of fractionator vent gases would also be a worthwhile project. All of these can best be carried out by today's producers of formaldehyde.

I. Introduction

Formaldehyde was first produced in the U. S. in 1901, at that time its chief use was as an embalming agent and disinfectant. Today, some seventy odd years later production capacity exceeds seven and one half billion pounds per year, [5] with approximately two thirds of the production utilized in the formulation of various synthetic resins.

Formaldehyde is normally marketed in aqueous solutions containing from 36 to 50 weight percent formaldehyde. The standard (USP) solution is 37 percent, although large scale industrial users prefer a nominal 50 percent solution. Formaldehyde solutions usually contain sufficient methanol to prevent precipitation of polymer during storage and shipping, although precipitation may be prevented in solutions containing relatively small amounts of methanol by keeping the solution warm.

Formaldehyde is produced principally from methanol. Two processes are dominant in the U. S. today, the mixed oxide catalyzed process and the silver crystal (or gauze) catalyzed process.

The primary licensors of the mixed oxide process are Reichhold and Lummus, while ICI and Borden prevail in the licensing of the silver process. The silver catalyzed process is the subject of this report.

A third process, based on the partial oxidation of light hydrocarbons, had been utilized by Celanese at their large Bishop, Texas plant until quite recently. That particular facility at Bishop has now been shutdown and replaced by a silver process unit. With national energy source demands escalating feedstock costs for the partial oxidation process, it is extremely doubtful that any new facility in the U. S. will again employ this process.

Atmospheric emissions generated by the silver catalyst process are associated primarily with the absorber vent gas stream. Minor quantities of hydrocarbons may be discharged by steam ejectors on the product fractionator. Additionally, small quantities of spent caustic or waste water may be produced.

Today an estimated 77%* of U.S. formaldehyde capacity is based on the silver catalyst process. This is appreciably more than its estimated share of 61% in 1969.[4] A large part of this increase is due to Celanese switching to the silver process, but even discounting that situation, the capacity of the silver-catalyzed process appears to be increasing at a faster rate than does the capacity of the mixed oxide process. If the silver process can maintain its present share of the total formaldehyde capacity, it will expand to 1.2×10^{10} lbs./year in 1985.

*About 5.9×10^9 lbs./year.

II. Process Description

Despite the fact that formaldehyde was produced from methanol over one hundred years ago (in 1868 by A. W. Hofmann), the chemistry - of the silver catalyzed process - is still in dispute. It is thought that the reaction involves either the dehydrogenation of methanol (EQ. 1) followed by the oxidation of hydrogen (EQ. 2A).

(1) $CH_3OH \rightleftharpoons CH_2O + H_2$

(2A) $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$

or a combination of methanol dehydrogenation (EQ. 1) and methanol oxidation (EQ. 2B)

(1) $CH_3OH \rightleftharpoons CH_2O + H_2$

(2B) $CH_3OH + \frac{1}{2} O_2 \longrightarrow CH_2O + H_2O$

Regardless of this controversy, the implementation of the process is relatively simple and quite straightforward, as evidenced by the following brief process description (which may be more easily followed by referring to the Figure FS-1 flow sheet):

Prior to its admixture with methanol vapors, air is caustic washed to remove CO_2 and trace sulfur compounds - the latter of which will poison the silver catalyst. The air is then heated to about 150° F.

Fresh methanol and recycle methanol are combined, vaporized and then superheated to approximately 170° F. Heat is supplied by either exchange with the converter effluent or medium pressure steam.

The heated air and superheated methanol vapors are combined in such proportions that the oxygen/methanol mole ratio is about 1:4. (Decreasing the percentage of methanol in the mixture decreases conversion while increasing yield; however, methanol must comprise more than 37 percent by volume of the mixture to avoid the explosive area. Increasing the amount of methanol increases conversion and decreases yield.) The air/methanol mixture is induced into a battery - sometimes about three - of catalytic converters. Upon passing through the silver catalyst, the net exotherm generated heats the vapors to about 1175° F. This temperature is maintained either by varying the air/methanol ratio or by means of combination heating and cooling coils located within the converters. The hot effluent gases must be quenched to avoid decomposing the formaldehyde. This is generally accomplished solely within the primary absorber, which is close-coupled with the converters, but feed vs effluent heat exchange is utilized - in part - by some plants.

The primary absorber is a packed tower. The primary absorption liquid - and quench - for the formaldehyde and unreacted methanol vapors is the so-called "F-M Liquor". This liquor is an aqueous solution containing about 28 to 30 percent formaldehyde and 20 to 22 percent methanol. Part of the FM liquor is withdrawn from the bottom of the primary absorber, pumped through a water cooled exchanger, and recirculated to the top of the primary absorber. The remainder of the FM liquor is withdrawn from the bottom of the absorber and pumped to intermediate storage. Uncondensed vapors and non-condensibles are withdrawn from the top of the primary absorber and 'blown' into the secondary absorber.

The secondary absorber recovers the major portion of the uncondensed vapors by providing the necessary contact between the vapors and cool distilled water, which is introduced onto the top tray of the secondary absorber. The top of the tower is maintained at about 75° F to 80° F by providing additional cooling via secondary coolers for the upper tray section. This minimizes hydrocarbon loss via the relatively large non-condensible overhead vent. The weak formaldehyde/methanol solution withdrawn from the bottom of the secondary absorber is pumped to the primary absorber and used as make-up.

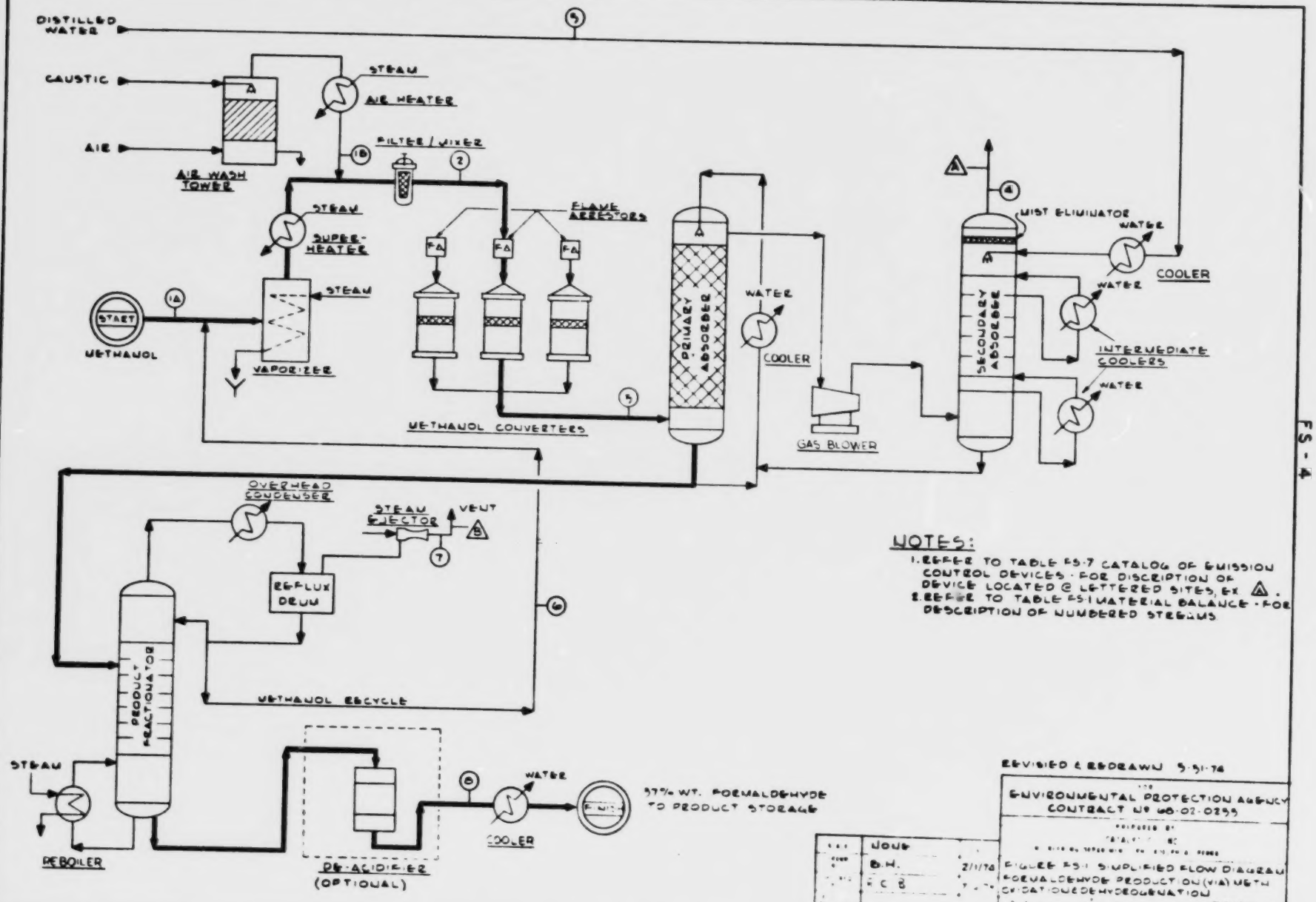
The FM liquor in the intermediate storage or surge tank is pumped to the product fractionator - a vacuum column. Here pure (99 + %) methanol is taken as overhead product and recycled to either methanol storage or to the vaporizer. The bottom product is a nominal 37 wt. % solution of formaldehyde, containing less than 1% methanol. This solution may be treated for removal of trace amounts of formic acid prior to storage. Polymer formation and precipitation in storage is prevented either by the addition of supplemental methanol, by providing heated storage, or by both,

Table FS-1 presents a typical material balance for silver process formaldehyde production. Absorber vent gas composition is based on a combination of published data [1] and questionnaire responses, whereas the below-listed yields, etc., are representative of published data only:[8]

	Mole %
Methanol in air/methanol feed mixture	44
Methanol conversion	65
Formaldehyde yield (Fresh Feed Basis)	89

Table FS-1 material balance relates to an average size plant (100 MM lbs./year of 37% formaldehyde). This typical unit will be used in economic studies discussed later in this report. Table FS-2 presents the same material balance with quantities expressed as tons per ton of 37% formaldehyde.

Table FS-3 presents an estimated heat balance around the converter section.



NOTES:

1. REFER TO TABLE FS-7 CATALOG OF EMISSION CONTROL DEVICES - FOR DISCRIPTION OF DEVICE LOCATED @ LETTERED SITES, EX △.
2. REFER TO TABLE FS-1 MATERIAL BALANCE - FOR DESCRIPTION OF NUMBERED STREAMS

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PREPARED BY
[illegible]

DRWN	JOHN	
CHKD	D.H.	2/1/74
APPD	F.C.B.	

FIGURE FS-1 SIMPLIFIED FLOW DIAGRAM FORMALDEHYDE PRODUCTION (VIA) METH OXIDATIVE DEHYDROGENATION

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FS-4

TABLE FS-1

TYPICAL MATERIAL BALANCE FOR

SILVER CATALYST PROCESS FORMALDEHYDE PLANT

PRODUCING 100 MM LBS./YR. OF 37% FORMALDEHYDE

Stream No.	1	2	3	4	5	6	7	8
Component	Fresh Feed	Total Feed	Methanol Converter Effluent	Absorber Vent Gas	Absorber Make-up Water	Fractionator Overhead Liq. (Recycle)*	Fractionator Off-Gas **	Product
Formaldehyde			4,546	7			4	4,535
Methanol	5,429	8,181	2,853	31		2,752	10	60
Hydrogen			123	123				
Carbon Dioxide			558	558				
Carbon Monoxide			64	64				
Water			2,160	178	5,678			7,660
Oxygen	2,161	2,161	38	38				
Nitrogen	7,147	7,147	7,147	7,147				
Total - Lbs./Hr.	14,737	17,489	17,489	8,146	5,678	2,752	14	12,255

*Also includes unknown (but very small) amount of formaldehyde.

**Also includes air, water vapor and ejector steam.

TABLE FS-2

TYPICAL MATERIAL BALANCE

FOR

SILVER CATALYST PROCESS FORMALDEHYDE PLANT

UNITS - TON/TON OF 37% FORMALDEHYDE

Stream I. D. No.	1 (A & B)	2	3	4	5	6	7	8
	Fresh Feed	Total Feed	Methanol Converter Effluent	Absorber Vent Gas	Absorber Make-up Water	Product Fractionator Vent*	Product	Product Fractionator Liq. Ovhd - Recycle**
Formaldehyde			.3709	.0006		.0003	.3700	
Methanol	.4430	.6675	.2328	.0025		.0008	.0050	.2245
Hydrogen			.0100	.0100				
Carbon Dioxide			.0455	.0455				
Carbon Monoxide			.0052	.0052				
Water			.1763	.0145	.4632		.6250	
Oxygen	.1763	.1763	.0031	.0031				
Nitrogen	.5832	.5832	.5832	.5832				
Total	1.2025	1.4270	1.4270	.6646	.4632	.0011	1.0000	.2245

*Also contains steam from ejector (when used) and water vapor and air from leakage.

**Contains unknown amount of formaldehyde.

TABLE FS-3
FORMALDEHYDE PRODUCTION
VIA
SILVER CATALYST PROCESS

GROSS HEAT BALANCE - CONVERTER SECTION ONLY

Heat In	BTU/Lb. of 37% Formaldehyde
Air Heater	23
Methanol heater, vaporizer and superheater	364
Exothermic heat of reaction	1,022
Total	1,409

Heat Out	
Converter temperature control	100
Endothermic heat of reaction	441
Converter effluent quench plus enthalpy residual (above base temp.)	868
Total	1,409

Note:

(1) Based on air/methanol and oxidation/dehydrogenation ratios shown in Table FS-1.

(2) Converter temperature - 1175° F.

(3) Base temperature - 60° F.

III. Manufacturing Plants and Emissions

Table FS-4 presents a list of U. S. plants producing formaldehyde. Production via the silver process is distributed among over thirty different plants, ranging in size from 25 to 1300 MM lbs./year. The relatively large number of plants results from the economy of captive production, whereby consumers find it more attractive to produce formaldehyde than to buy it. Concentrations of formaldehyde plants; therefore, are to be found in the same geographical areas as are the formaldehyde consuming industries. These locations include the Pacific Northwest, the Metropolitan Northeast, Texas and the lumber producing areas of the south.

Table FS-5 shows individual plant capacity figures and atmospheric emission data for the various formaldehyde plants surveyed in this study. The plants included in the tabulation range in capacity of from 40 to 855 MM lbs./year and represent about 1/3 of the total U. S. installed silver process capacity. Emissions from these plants are as follows:

A. Continuous Air Emissions

1. Absorber Vent

The emissions from this vent constitute the most important source of air pollution associated with the production of formaldehyde. Indeed, many respondents report it as their sole source of noxious emissions.

The composition of the absorber vent stream varies somewhat with catalyst age or activity. The normal range in composition (excluding for the moment uncondensed hydrocarbons) is*:

Component	Vol. % (Dry Basis)
CO_2	4.8 to 5.5
CO	0.2 to 0.6
CH_4	0.3 to 0.4
O_2	0.3
H_2	20.2 to 17.5
N_2	74.2 to 75.7

These reaction by-products transport varying quantities of hydrocarbons to the atmosphere when they are vented. Respondents report the following hydrocarbon emissions are associated with their absorber vents.

Component	Amount Lb./Lb. of 37% HCHO
Formaldehyde	0 to .001
Methanol	0 to .004
Methyl Formate	0 to .008
Methylal	0 to .001

A more complete summary of these emissions is listed in Table FS-6, representing a selected number of silver catalyst process plant operators.

*"Formaldehyde" - 3rd Edition, ACS Monograph Series, pp 18

TABLE FM-4
SUMMARY OF U. S. FORMALDEHYDE PLANTS

NOTE: The following tabulation of formaldehyde producers indicates published production capacity (MM lbs./year) by company, location and process. Determination of the process utilized was by combination of published information, questionnaire responses and private communications.

Company	Location	Silver Process	Metal Oxide Process
Allied	Ironton, Ohio	308	
Borden			
	Demopolis, Ala.	80	
	Diboll, Texas	70	
	Fayetteville, N. C.	200	
	Fremont, Calif.	80	
	Kent, Wash.	70	
	La Grande, Oregon	40	
	Louisville, Ky.	70	
	Missoula, Mont.	80	
	Sheboygan, Wisc.	120	
	Springfield Oregon	260	
Celanese	Bishop, Texas	1300	
	Newark, N. J.		117
	Rock Hill, S. C.		117
Commercial Solvents	Sterlington, La.	30	
	Seiple, Pa.	80	
Du Pont	Belle, W. Va.	485	
	Gresselli, N. J.	150	
	Healing Spring, N. C.	200	
	La Porte, Texas	200	
	Toledo, Ohio	320	
	Linden, N. J.	150	
GAF	Calvert City, Ky.		100
Georgia Pacific	Columbus, Ohio		100
	Coos Bay, Oregon		80
	Crosett, Ark.	100	60
	Albany, Oregon		100
	Taylorsville Miss.		100
	Vienna, Ga.	100	
Gulf	Vicksburg, Miss.		40
Hercules	Louisiana, Mo.	170	
	Wilmington, N. C.	95	
Hooker	N. Tonawanda, N. Y.	135	
Monsanto	Alvin, Texas	150	
	Addyston, Ohio	110	
	Eugene, Oregon	100	
	Springfield, Mass.	280	

TABLE FM-4 CONTINUED
SUMMARY OF U.S. FORMALDEHYDE PLANTS

Company	Location	Silver Process	Metal Oxide Process
Reichhold	Hampton, S.C.	36	
	Houston, Texas		100
	Moncure, N.C.		100
	Tacoma, Wash.		40
	Tuscaloosa, Ala.	70	
	Kansas City, Kansas	40	
	White City, Oregon		50
	Malvern, Ark.		100
Rohm & Haas	Philadelphia, Pa.	25	
Skelly	Springfield, Oregon		70
	Winfield, La.		70
Tenneco	Fords, N.J.	105	160
	Garfield, N.J.	105	
Union Carbide	Bound Brook, N.J.		150
Wright	Acme, N.C.		75
Total Process Capacity - MM Lbs./Year =		5,914	1,729*
Number of Plants =		35	19
Average Plant Size - MM Lbs./Year =		169	91
Capacity of Total Industry - MM Lbs./Year =		7,643	
Percent of Total Industry Capacity =		77.4	22.6

*Most recent total reported

TABLE FS-5
NATIONAL EMISSIONS INVENTORY
FORMALDEHYDE VIA SILVER CATALYST PROCESS

EPA Code Number	14-1		14-3
Date on-stream			
Capacity - Tons of 37% HCHO/Yr.	154,000		47,500
Average Production - Tons of 37% HCHO/Yr.			47,500
Range in Production - % of Max.	17		0
Emissions to Atmosphere			
Stream	Absorber Vent	Converter Emergency Vent	Converter Start-up Vent
Flow - lbs./hr.	Not Specified	Not Specified	2620
Flow Characteristic - Continuous or Intermittent	Continuous	Intermittent	Intermittent
if Intermittent - hrs/yr.		0.10	5
Composition - Tons/Ton of 37% HCHO			
Formaldehyde		+	
Methanol		+	.00011
Methyl Formate			
Di-methyl Ether			
Methylal			
Oxygen			
Nitrogen			
Carbon Monoxide			
Carbon Dioxide			
Methane	+		
Water			
Hydrogen	+	+	.00003
Sample Tap Location	None	None	None
Date or Frequency of Sampling	Never	Never	Never
Type of Analysis			
Odor Problem	No		
Vent Stacks	Yes	Not Specified	Not Specified
Flow - SCFM per stack			
Number	1		
Height - Feet (elev. @ tip)	43.8		
Diameter - Inches	42		
Exit Gas Temperature - F°		>500°	
Emission Control Devices	Yes	No	No
Type - Water Scrubber	X		
Incinerator			
Catalog I. D. No.	FS-1		
Total Hydrocarbon Emissions - Ton/Ton HCHO (37%)	Not Specified		.00489
Total Particulate & Aerosol Emissions - Ton/Ton HCHO (37%)			0
Total NO_x - Ton/Ton HCHO (37%)			0
Total SO_x - Ton/Ton HCHO (37%)			0
Total CO - Ton/Ton HCHO (37%)			.00159

Absorber Vent
Not Specified
Continuous
.00114
.00364
+
+
.00159
+
.01193
.00755
Yes
718
1
6.668
.67
82°
No

TABLE FS-5

NATIONAL EMISSIONS INVENTORY

FORMALDEHYDE VIA SILVER CATALYST PROCESS

EPA Code No.		14-4		
Date on-stream				
Capacity - Tons of 37% HCHO/Yr.		52,500		
Average Production - Tons of 37% HCHO/Yr.		52,500		
Range in Production - % of Max.		0		
Emissions to Atmosphere				
Stream	Absorber #1 Vent	Absorber #2 Vent	Absorber #3 Vent	Stripper Overhead Vent
Flow - lbs./hr.	4040	1350	4040	54
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous
if Intermittent - hrs./yr.				
Composition - Tons/Ton of 37% HCHO				
Formaldehyde	.00035	.00012	.00035	.00002
Methanol	.00111	.00037	.00111	.00005
Methyl Formate				
Di-methyl Ether				
Methylal	.00269	.00090	.00269	+
Oxygen	.25569	.08523	.25569	+ .00372
Nitrogen	.00238	.00080	.00238	
Carbon Monoxide	.03354	.01115	.03354	+
Carbon Dioxide				
Methane	.00946	.00315	.00946	.00038
Water	.00523	.00174	.00523	
Hydrogen				
Sample Tap Location	None		None	None
Date or Frequency of Sampling	Never	Never	Never	Never
Type of Analysis	Calc.	Calc.	Calc.	Estimate
Odor Problem	No	No	No	No
Vent Stacks	Yes	Yes	Yes	Yes
Flow - SCFM per stack	1090 to 1152	363 to 384	1090 to 1152	5 to 20
Number	1	1	1	1
Height - Feet (elev. @ tip)	60	50	65	65
Diameter - Inches	.9	.6	9	4
Exit Gas Temperature - F°	104° to 140°	104° to 140°	104° to 140°	78° to 110°
Emission Control Devices	No	No	No	+
Type - Water Scrubber				
Incinerator				
Catalog I. D. No.				FS-5
Total Hydrocarbon Emissions - Ton/Ton HCHO (37%)		.00348		
Total Particulate & Aerosol Emissions - Ton/Ton HCHO (37%)		0		
Total NO_x - Ton/Ton HCHO (37%)		0		
Total SO_x - Ton/Ton HCHO (37%)		0		
Total CO - Ton/Ton HCHO (37%)		.00556		

TABLE FS-5
NATIONAL EMISSIONS INVENTORY
FORMALDEHYDE VIA SILVER CATALYST PROCESS

EPA Code Number	14-7	14-8		14-9	
Date on-stream					
Capacity - Tons of 37% HCHO	50,000	75,000		30,919	
Average Production - Tons of 37% HCHO		75,000		30,919	
Range in Production - % of Max.	0	0		0	
Emissions to Atmosphere					
Stream	Absorber Vent	Absorber Vent	Jet Exhaust	Absorber Emerg. Vents Manual/Auto	Absorber Vent
Flow - lbs./hr.	7369	11,600	6		Not Specified
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Intermittent	
if Intermittent - hrs./yr.					
Composition - Tons/Ton of 37% HCHO					
Formaldehyde	.00035				
Methanol	.00340	.00067	.00033		
Methyl Formate	.00230				
Di-methyl Ether					
Methylal					
Oxygen				+	
Nitrogen	.53000	.56129		+	
Carbon Monoxide	.00100	.00529		+	
Carbon Dioxide	.03850	.05920		+	
Methane					
Water	.02750	.00634			
Hydrogen	.01100	.01263		+	
Sample Tap Location	None	Stack	None	Process	
Date or Frequency of Sampling	Never	1972	Never	Random	
Type of Analysis	Calc'd. ex Design	GLC + Titration	Calc'd.	Orsat + ?	
Odor Problem	No	No	No	No	
Vent Stacks	Yes	Yes	Yes	Yes	
Flow - SCFM per stack	2000	3200			
Number	1	1	1	1/1	
Height - Feet (elev. @ tip)	98	100	43	30/20	
Diameter - Inches	8	16	1.5	8/8	
Exit Gas Temperature - F°	95	54	200	50°/50°	
Emission Control Devices	Yes	Yes	Yes	No	Yes
Type - Water Scrubber					
Incinerator					+
Demister	+	+			
Other			+ (condenser)		
Catalog I. D. No.	FS-3	FS-5	FS-9		FS-2
Total Hydrocarbon Emissions - Ton/Ton of 37% HCHO	.00605	.00100		Not Specified	
Total Particulate & Aerosol Emissions - Ton/Ton of 37% HCHO	0	0			
Total NO_x Emissions - Ton/Ton of 37% HCHO	0	0			
Total SO_x Emissions - Ton/Ton of 37% HCHO	0	0			
Total CO Emissions - Ton/Ton of 37% HCHO	.00100	.00529			

TABLE FS-5
NATIONAL EMISSION INVENTORY
FORMALDEHYDE VIA SILVER CATALYST PROCESS

EPA Code Number	14-10	14-9
Capacity - Tons of 37% HCHO/Yr.	240,000	200,000
Average Production - Tons of 37% HCHO/Yr.		
Range in Production - % of Max.	0	0
Emissions to Atmosphere		
Stream	Absorber Vent Incinerator Flue gas	Not Specified
Flow - lbs./hr.	39,727	
Flow Characteristic - Continuous or Intermittent	Continuous	
if Intermittent - hrs./yr.		
Composition - Tons/ton of 37% HCHO		
Formaldehyde	TR	
Methanol	TR	
Methyl Formate		
Di-methyl Ether		
Methylal		
Oxygen	.01005	
Nitrogen	.47940	
Carbon Monoxide		
Carbon Dioxide	.04269	
Methane		
Water	.18491	
Hydrogen	TR	
Sample Tap Location		
Date or Frequency of Sampling	Never	
Type of Analysis	CLC	
Odor Problem	No	
Vent Stacks	Yes	
Flow - SCFM per stack	10,050	
Number	1	
Height - Feet (elev. @ tip)	85	
Diameter - Inches	60	
Exit Gas Temperature - F°	900	
Emission Control Devices	Yes	Yes
Type - Water Scrubber		
Incinerator	+	+ Boiler
Catalog I. D. Number	FS-7	FS-8
Total Hydrocarbon Emissions - Ton/Ton HCHO (37%)	0	Cannot Be Determined
Total Particulate & Aerosol Emissions - Ton/Ton HCHO (37%)	0	
Total NO_x - Ton/Ton HCHO (37%)	0	
Total SO_x - Ton/Ton HCHO (37%)	0	
Total CO - Ton/Ton HCHO (37%)	0	

TABLE FS-5
NATIONAL EMISSIONS INVENTORY
FORMALDEHYDE VIA SILVER CATALYST PROCESS

EPA Code No.	14-12	14-18		14-20	
Date on-stream					
Capacity - Tons of 37% HCHO	35,000	20,000		50,000	
Average Production - Tons of 37% HCHO	35,000	20,000		50,000	
Range in Production - % of Max.	0	0		0	
Emissions to Atmosphere					
Stream	Absorber Vent	Jet Exhaust	Absorber Vent	Absorber Vent	Distillation Tower Overhead Vent
Flow - lbs./hr.	5,855	1000	3360	7386	30
Flow Characteristic - Continuous or Intermittent	Continuous	Continuous	Continuous	Continuous	Continuous
if Intermittent - hrs./yr.					
Composition - Tons/Ton of 37% HCHO					
Formaldehyde	.00041			.00035	.00120
Methanol	.00082			.00326	.00120
Methyl Formate				.00224	
Di-methyl Ether					
Methylal					
Oxygen			.00250		
Nitrogen			.54828	.51016	
Carbon Monoxide	.00276		.00292	.00104	
Carbon Dioxide			.05856	.03688	
Methane	.00191		.00167		
Water		.18519		.02656	
Hydrogen	.01390		.00989	.01040	
Sample Tap Location		None	Top of Tower		
Date or Frequency of Sampling	Daily	Never	Bi-annual	Random	Never
Type of Analysis	Calc'd.		Orsat + ?	Calc'd	Not Specified
Odor Problem		No	No	No	No
Vent Stacks	Yes	Yes	Yes	Yes	
Flow - SCFM per stack	.460		891		
Number	1	1	1	1	1
Height - Feet (elev. @ tip)	73	22	44	95	95
Diameter - Inches	18	1	6	132	132
Exit Gas Temperature - F°	80	200	50	95	95
Emission Control Devices	Yes	No	No	No	No
Type - Water Scrubber					
Incinerator					
Demister	+				
Other					
Catalog I. D. No.	FS-4				
Total Hydrocarbon Emissions - Ton/Ton of 37% HCHO	.00123	0		.00825	
Total Particulate & Aerosol Emissions - Ton/Ton of 37% HCHO	0	0		0	
Total NO_x Emissions - Ton/Ton of 37% HCHO	0	0		0	
Total SO_x Emissions - Ton/Ton of 37% HCHO	0	0		0	
Total CO Emissions - Ton/Ton of 37% HCHO	.00276	.00292		.00104	

TABLE (5a-)

NATIONAL EMISSIONS INVENTORY

FORMALDEHYDE VIA SILVER CATALYST PROCESS

Page [illegible] of [illegible]

EPA Code No.			14-11		14-20	
Date on-stream						
Capacity - Tons of 37% HCHO/Yr.			427,500		50,000	
Average Production - Tons of 37% HCHO/Yr.					50,000	
Range in Production - % of Max.			0		0	
Emissions to Atmosphere						
Stream			Absorber Vent		Absorber Vent	Distillation Column Overhead Vent
Flow - Lbs./Hr.			54,660		734	30
Flow Characteristic - Continuous or Intermittent			Continuous		Continuous	Continuous
if Intermittent - Hrs./Yr.						
Composition - Tons/Ton of 37% HCHO						
Formaldehyde			< .00001		.00035	.00120
Methanol			.00076		.0324	.00120
Methyl Formate			.00829		.0022+	
Di-methyl Ether						
Methylal			.00120			
Oxygen						
Nitrogen			.39+975		.51016	
Carbon Monoxide			.021040		.00104	
Carbon Dioxide			.09209+		.03+88	
Methane			.00012+			
Water					.02+5+	
Hydrogen			.01+271		.01040	
Sample Tap Location			Ground level			
Date or Frequency of Sampling			Daily		Random	Never
Type of Analysis			Chromatograph		Calc'd.	Not Specified
Odor Problem			No		No	No
Vent Stacks			Yes		Yes	
Flow - SCFM per stack	4700	3+00	10,000			
Number	1	1	1		1	1
Height - Feet (elev. @ tip)	90	93	95		95	95
Diameter - Inches	10	12	14		132	132
Exit Gas Temperature - F°	50	50	50		95	95
Emission Control Devices		No			No	No
Type - Water Scrubber						
Incinerator						
Catalog I. D. No.						
Total Hydrocarbon Emissions - Ton/Ton HCHO (37%)			.01025		.00825	
Total Particulate & Aerosol Emissions - Ton/Ton HCHO (37%)					0	
Total NO_x - Ton/Ton HCHO (37%)					0	
Total SO_x - Ton/Ton HCHO (37%)					0	
Total CO - Ton/Ton HCHO (37%)			.02101		.00104	

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TABLE FS-6
TYPICAL ABSORBER VENT GAS COMPOSITION FOR 100 MM LB./YR. (E) FORMALDEHYDE PLANT

SILVER CATALYST PROCESS

Component	Normal Range in Composition ex Source "A" Vol % (A)	Normal Range in Composition ex Source "B" Vol % (B)	Average Flow Rate and Composition (F) Mole %	MPH	LB./HR.
Formaldehyde		0 to 0.5	0.07	0.24	7
Methanol		0 to 0.9	0.28	0.96	31
Hydrogen	17.5 to 20.2	13.0 to 27.0	17.72	60.79	123
Carbon Dioxide	4.8 to 5.5	0 to 7.0	3.69	12.67	558
Carbon Monoxide	0.2 to 0.6	0.1 to 2.8	0.66	2.28	64
Oxygen	0.3	0 to 1.0	0.35	1.19	38
Nitrogen	74.2 to 75.7	67.0 to 75.7	74.35	255.07	7147
Methane	0.3 to 0.4	0 to 0.4 (D)	0	0	0
Water		0 to 6.6	2.88	9.86	178
Methyl Formate		0 to 0.80	0	0	0
Methylal		0 to 0.12 (C)	0	0	0
Methoxy Methylal		0 to 0.01 (C)	0	0	0
Dimethyl Ether		0 to 0.01 (C)	0	0	0
	Totals		100.00	343.06	8146

NOTES

(A) Source "A" is 3rd edition of ACS Monograph on "Formaldehyde", page 18.
(B) Source "B" listing shows lowest and highest limits of normal range, as reported by questionnaire respondents.
(C) Reported by one respondent only.
(D) Reported by two respondents.
(E) Of 37% formaldehyde.
(F) Based on weighted average of component concentrations as reported by questionnaire respondents and applied to flow rate for "typical" 100 MM lbs./year facility (see Table FS-1).

2. Product Fractionator Ejector Exhaust

It is believed that all product fractionators are operated at sub-atmospheric pressures. Therefore, the use of either steam ejectors or vacuum pumps is required. Four respondents reported emissions from this source, but only three (EPA Code No's. 14-4, 14-8 and 14-20) reported the emission of noxious compounds. The emissions from the ejectors are listed in Table FS-5.

B. Intermittent Air Emissions

1. Converter Start-Up Vent

The operator of plant EPA Code No. 14-3 reported emissions from this source and stated that, "during start-ups the feed to the converter is vented to the atmosphere until stabilized and then switched gradually into the reactor. Total vent time is about 30 minutes. There are about 10 start-ups per year". Data provided by the respondent indicate that this operation results in the emission of .0001 lbs. of hydrocarbons/lb. of formaldehyde.

Start-up vents of a different nature were reported by respondents 14-6 and 14-9, both of whom burn their absorber tail gases in the boiler house. During start-ups, until the tail gas composition and flow have stablilized, the tail gas is vented to the atmosphere. After this period the tail gas is cut to the boiler house and burned. No estimate was given of the emissions resulting from this operation, but they should be negligible.

2. Converter Emergency Vent

Again, only operator 14-3 reported emissions from this source. Lack of data prevents the calculation of emission rates, but the infrequency and short duration of the emission preclude its characterization as a significant emission source.

C. Continuous Liquid Wastes

1. Waste Water

The production of various waste water streams have been reported as follows:

Plant 14-3 - .030 gallons/lb. of 37% formaldehyde or 360 gallons/hour. The waste is treated on plant in an extended aeration biological treatment plant.

Plant 14-7 - 62,500 gallons/hour of cooling water. 'Treated' on plant.

Plant 14-8 - 120 gallons/hr. from the waste heat boiler blowdown plus 4500 gallons/hour from the cooling tower blowdown.

Plant 14-20 - 7,500 gallons/hour cooling tower blowdown. Treated in plant.

2. Spent Caustic

While no operator reported the generation of spent caustic, it seems reasonable to surmise that most plants do produce small quantities of this substance as a result of their air washing operation.

D. Intermittent Liquid Wastes

1. Ion Exchange Regeneration

Presumably most operators remove formic acid from product formaldehyde via an ion exchange resin system. Such systems are normally regenerable by intermittent back-flushing procedures, which would produce an intermittent waste liquid stream. Operator 14-10 reports that every six to 20 days a weak aqueous solution containing about 0.4 percent formic acid and 1.5 percent formaldehyde is discharged to the waste treatment plant as a result of this operation. Flow rates are not given. Operator 14-3 shows such a waste stream on this block flow diagram, but gives no further details in the body of his response.

2. Methyl Formate Removal

One operator reported privately that it was his practice to remove methyl formate from stored formaldehyde. Presumably, this would result in the production of a small intermittent liquid waste stream. It is believed that this operation is atypical of the industry.

E. Solid Wastes

All respondents to the silver process questionnaire reported that their facility produced no solid waste material.

F. Odors

None of the respondents reported receiving any odor complaints during the past year. Half of the respondents, however, did report that odors are occasionally detectable at the plant site. The odoriferous materials were identified as formaldehyde and methanol.

All operators reporting odors mentioned the absorber vent as at least one of the sources. In addition, operators 14-3 and 14-8 identified the product fractionator as a source.

G. Fugitive Emissions

Only the operator of plant 14-3 has offered a quantitative estimate of fugitive emissions. His estimate is 30 lbs./hr. or .00025 lbs./lb. All other operators state that fugitive emissions are either nil or quite small. As operator 14-4 summarizes the situation, "minor losses of formaldehyde and/or methanol occur mainly due to leaks in pump seals and occasional piping leaks. The actual amount is considered negligible and most likely will not show in material balance calculations."

IV. Emission Control Devices and Systems

A. Emission Controls on Absorber Vent

1. Devices Currently Employed

Excluding the ever-present mist eliminator in the top of the secondary absorber, the majority of U.S. plants do not employ emission control devices. Those that do, invariably utilize some type of combustion device. Plant 14-6 and 14-9 both burn their tail gases in the fire box of a steam boiler. Details of design, performance and cost are considered by the respondents to be proprietary, however, they intend to offer the unit to the industry on a licensing arrangement. Plant 14-10 has installed a (thermal) 'fume abatement' unit, which in their opinion "represents the latest technical art". Actual performance data for the fume abatement unit are lacking, however, the respondent reports that data extrapolated from pilot unit runs indicate that combustion is close to 100 percent. Plant 14-1 utilizes a 'waste gas incinerator', again performance is estimated rather than measured. The cost and performance details that have been reported on these devices are listed in Table FS-7.

(a) Thermal Incinerators

Table FS-8 presents a material balance for this type of control device. The data in the table are based on a 1750° F combustion zone temperature and 4 mole % oxygen (dry basis) in the stack gas, this should normally assure complete combustion of pollutants on a self-sustaining basis (i.e., no auxiliary fuel). However, there maybe some periods of operation when the vent gas is at the lean end of its composition, thus requiring auxiliary fuel.

Although there are several tail gas incinerators extant, no actual performance data were provided by the questionnaire respondents. Available information indicates that combustion efficiency should be quite high - 99+%.

There are several problem areas with this type device. They are:

(1) Vent gas is available at low pressure.

(2) Because the gas has a low heating value (60 BTU/SCF on a dry basis), special incinerator designs must be utilized to assure self-sustenance.

(3) Flame control is difficult due to low heating value and low level of incandescence, therefore, flame-outs could be a problem.

(4) The stream has a relatively high hydrogen content which might cause some special hazards.

(b) Boiler House Burner

The heating value of the tail gas can be recovered, apparently economically, by utilizing the tail gas as a boiler house fuel supplement. Combustion would be expected to be essentially

TABLE FS-7
CATALOG OF EMISSION CONTROL DEVICES
FORMALDEHYDE VIA THE SILVER CATALYST PROCESS

ABSORBER/SCRUBBERS/MIST ELIMINATORS				
EPA Code No. for plant using	14-4	14-7	14-12	14-8
Flow diagram (Fig. I) stream I. D.	⚠	⚠	⚠	⚠
Device I. D. No.	FS-8	FS-3	FS-4	FS-5
Control Emission of	Formaldehyde & Methanol	Formaldehyde & Methanol	Formaldehyde & Methanol	Formaldehyde & Methanol
Scrubbing/Absorbing liquid	Water	N/A	N/A	N/A
Type - Spray				
Packed Column	1			
Column w/trays	2			
Number of trays	12 & 14			
Tray type	Bubble Cap			
Other		+ Demister	+ Demister	+ Demister
Scrubbing/Absorbing liquid rate - GPM	5	None	None	None
Design Temp. (Operating Temp.) F°			(80)	(54)
Gas Rate, SCFM (lb./hr.)		2,000	1,460	3,200
T-T Height, Ft.	8 to 15			
Diameter, Ft.	1 to 1.3			
Washed gases to stack	Yes	Yes	Yes	Yes
Stack height - Ft.		98	73	100
Stack Diameter - Inches		8	18	16
Installed Cost - Mat'l. & Labor - $	Not Available		5,000	700
Installed Cost based on - "year" - dollars	↓		1972	1971
Installed Cost - c/lb. of 37% HCHO - Yr.			.00714	.00047
Operating Cost - Annual - $ - 1972				400
Value of Recovered product, $/Yr.		1,440		0
Net Operating Cost - Annual, $				400
Net Operating Cost - c/lb. of 37% HCHO				.00027
Efficiency - % - SE*				
Efficiency - % - SERR*				
INCINERATION DEVICES				
EPA Code No. for plant using		14-1	14-6	14-9	14-10
Flow Diagram (Fig. I) stream I. D.		⚠	⚠	⚠	⚠
Device I. D. No.		FS-1	FS-6	FS-2	FS-7
Type of Compound Incinerated		Formaldehyde & Methanol	Formaldehyde & Methanol	Formaldehyde & Methanol	Formaldehyde & Methanol
Type of Device - Flare					
Incinerator		+			+
Other			+ Boiler	+ Boiler	
Material Incinerated, SCFM (Lb./Hr.)		Not Specified	3028		10,050
Auxilliary Fuel Req'd. (excl. pilot)			Yes	Yes	No
Type					
Rate - BTU/hr.					
Device or Stack Height - Ft.		43.75	Not Disclosed	Not Disclosed	85
Installed Cost - Mat'l. & Labor - $			↓	↓	200,000
Installed Cost based on - "year" - dollars					1972
Installed Cost - c/lb. of 37% HCHO					.04111
Operating Cost - Annual - $ (1972)					60,000
Operating Cost - c/lb. of 37% HCHO					.01233
Efficiency - % - CCR*		100			100
Efficiency - % - SERR*		100			100

*See Appendix for explanation of these items

TABLE FS-7
CATALOG OF EMISSION CONTROL DEVICES
FORMALDEHYDE VIA THE SILVER CATALYST PROCESS

CONDENSERS	
EPA Code No. for plant using	14-8
Flow Diagram Stream I. D.	Δ
Device I. D. No.	FS-9
Controls Emission of	Methanol
Primary Refrigeration Liquid	
Capacity of Refrigeration Unit - Tons	
Gas Rate - SCFM	
Temperature to Condenser - F°	
Temperature out of Condenser - F°	
Liquid Recovered - GPM	Unknown
Non-Condensibles - SCFM	131 Lb./hr.
Installed Cost - Mat'l. & Labor - $	3,300
Installed Cost based on - "year" - dollars	1971
Installed Cost - ¢/lb. of 37% HCHO/Yr.	.00220
Operating Cost - Annual - $ (1972)	2,000
Value of Recovered Products - $/Yr.	Unknown
Net Operating Cost - Annual - $	
Net Operating Cost - ¢/lb. of 37% HCHO	
Efficiency - % - SE*	
Efficiency - % - SERR*	

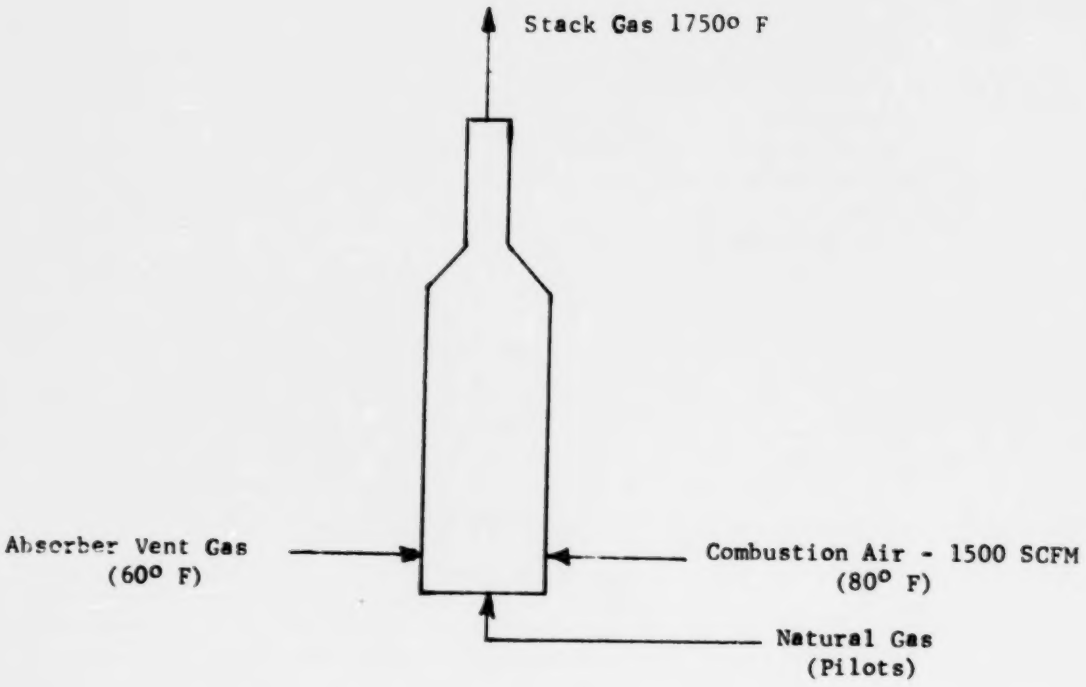
*See Appendix for explanation of these terms.

TABLE FS-8
THERMAL INCINERATOR
FOR
100 MM LB./YR. FORMALDEHYDE PLANT
ABSORBER VENT STREAM

OVERALL MATERIAL BALANCE - LB./HR.

Component	Absorber Vent Gas	Combustion Air	Flue * Gas
Formaldehyde	7		
Methanol	31		
Hydrogen	123		
Carbon Dioxide	558		711
Carbon Monoxide	64		
Oxygen	38	1614	590
Nitrogen	7147	5316	12463
Water	178	56	1368
Total	8146	6986	15132

*Excludes any NOx that may form as result of incineration, probably about 50 ppm.



complete, and thus, the emission level should be commensurate with that attained through the use of a thermal or catalytic incinerator. Actual performance data from the two units currently on-stream are considered to be proprietary.

2. Feasible Devices Not Currently Employed

It is assumed that these devices are not in use on current silver catalyst process plants, since they were not reported on questionnaires, at the public meeting nor in the literature.

(a) Plume Burner

This control device is distinguished from a flare stack by the definition that it does not normally require supplemental fuel. It would have the following limitations:

(1) Efficiency for removal of contaminants is less than for other combustion devices. The efficiency is influenced by the BTU content of the vent gas. Based upon qualitative data from similar control devices, it is estimated that 90 percent of CO and hydrocarbon pollutants will be burned.

(2) Small changes in vent gas composition could extinguish the burner if supplemental fuel and adequate instrumentation are not provided.

(b) Catalytic Incinerator

A conventional catalytic incinerator could reduce pollutants to levels similar to those attainable with a thermal unit. Although no existing formaldehyde plant is known to employ such a device, certain generalizations about design, operation and performance can be drawn from information available on similar applications.

It is estimated that a 900° F inlet temperature to the catalyst bed should be sufficient to obtain complete combustion of all hydrocarbon and carbon monoxide over standard noble metal catalysts. Maximum temperatures within the bed should be limited to 1200° F in order to prevent loss of catalyst activity through sintering and loss of surface area. This type of temperature control can be attained by permitting part of the process vent gas to by-pass the thermal combustion zone while co-currently employing excess air as quench between the thermal combustion zone and the catalyst bed. As the catalyst ages, combustion efficiency will decrease. With aged catalyst, it is expected that 10 to 15 percent of the feed combustibles will be vented to the atmosphere. Catalyst poisons, such as sulfur, will not normally be present in the process vent gas because they have previously been excluded to protect the main process silver catalyst. Table FS-9 presents a material balance for a catalytic incinerator with fresh catalyst.

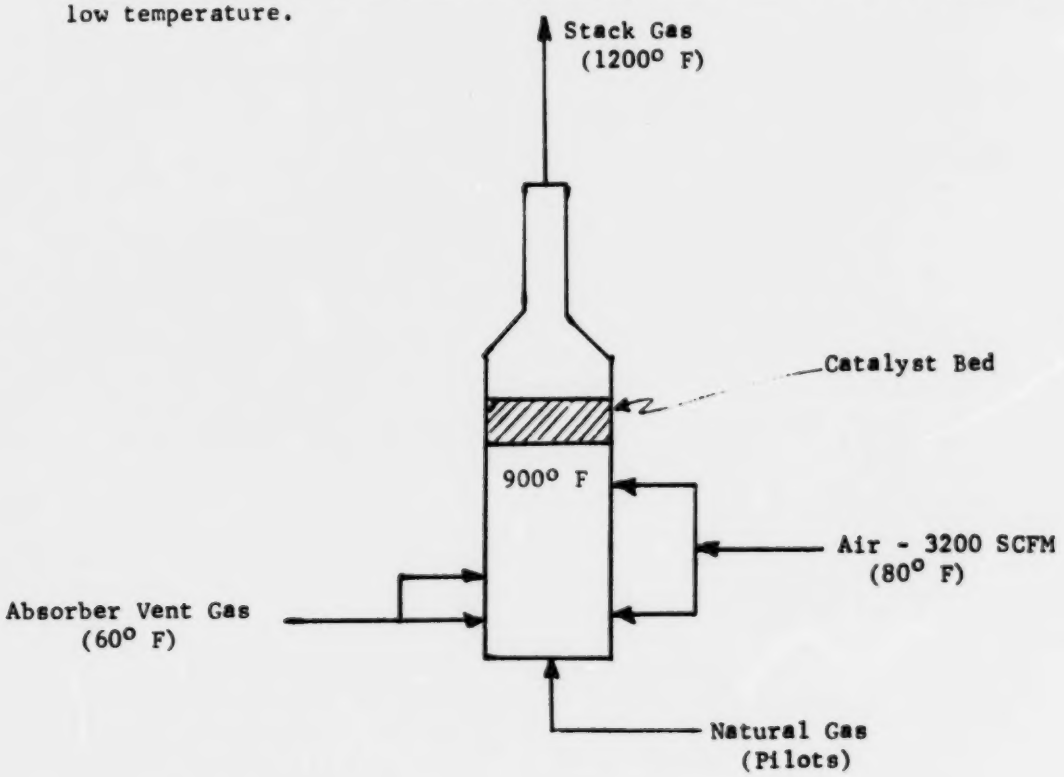
It is possible that NOx emissions from a catalytic incinerator will be less than those from a thermal incinerator since the

TABLE FS-9
CATALYTIC INCINERATOR
FOR
100 MM LB./YR. FORMALDEHYDE PLANT
ABSORBER VENT STREAM

OVERALL MATERIAL BALANCE - LB./HR.

Component	Absorber Vent Gas	Air to Incinerator	Flue* Gas
Formaldehyde	7		
Methanol	31		
Hydrogen	123		
Carbon Dioxide	558		711
Carbon Monoxide	64		
Oxygen	38	3429	2404
Nitrogen	7147	11286	18434
Water	178	118	1430
Total	8146	14833	22979

*Excludes NOx formation which is probably less than 50 ppm because of relatively low temperature.



homogenous oxidation of N_2 does not occur to any extent at 1200° F. Another possible advantage of the catalytic device is the lower requirement for supplemental fuel during periods of operation when the vent gas is abnormally low in heat content. On the debit side, operational costs can be expected to be 50 percent higher than for straight thermal devices.

(c) Water Scrubber

None of the silver process formaldehyde plants surveyed use water scrubbing. However, data are available from a mixed oxide catalyst formaldehyde plant, and that information was utilized to construct the water scrubber material balance presented in Table FS-10. A water scrubber requires less capital investment than any of the combustion devices except the plume burner. However, when compared to other aspects of thermal device considerations, scrubbers have the following disadvantages:

(1) Efficiency of removing hydrocarbons is less than for all the combustion devices except the plume burner.

(2) Efficiency of removing carbon monoxide is essentially zero.

(3) Air contaminants are transferred rather than destroyed, and thus require additional treatment or result in water pollution. This cost, however, is probably incremental on existing facilities.

(4) For all practical purposes, heat recovery from the tail gas is precluded.

B. Emission Controls on Product Fractionator Vent

1. Devices Currently Employed

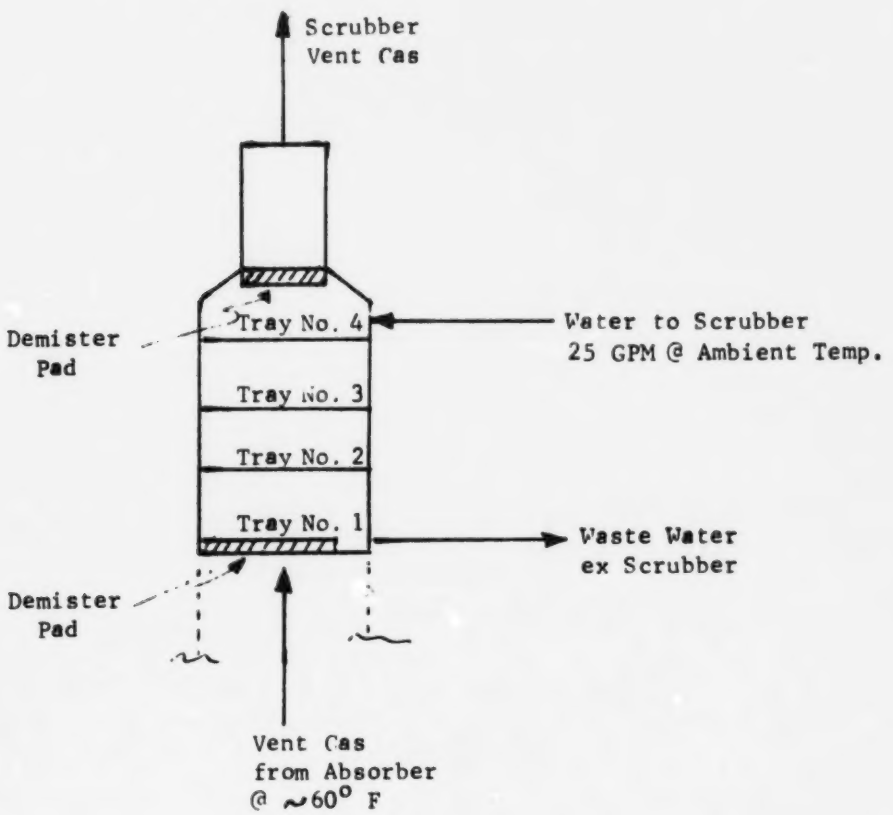
(a) Water Scrubber

The product fractionator operates at sub-atmospheric pressure, consequently the vent from that tower is normally through a steam powered vacuum ejector or vacuum pump. Most respondents maximize methanol recovery by cooling the suction line to the ejector or pump. For the purpose of this report, the jet or pump suction cooler is not considered a pollution control device. On this basis then only one questionnaire respondent has reported the use of a control device on this stream - operator 14-4. (However, it is understood that at least one plant recycles the discharge from the vacuum pump, which they utilize to effect the desired product fractionator operating pressure.) The device reported by respondent 14-4 consists of two water scrubbers in series, the first is a bubble cap column and the second is a packed column. Feed composition and flow are not available, thus efficiency cannot be calculated; however, based on uncontrolled emissions reported by other plants, efficiency is in the range of 79-97 percent. Admittedly, this results in, at best, a crude estimate of performance, but the unit is old and newer units could undoubtedly improve upon the actual performance. It does demonstrate that control of this stream by this method is practical. However, it suffers one drawback in that it transfers pollutants from one medium to another (i.e., air to water).

TABLE FS-10
WATER SCRUBBER
FOR
100 MM LB./YR. FORMALDEHYDE PLANT
ABSORBER VENT STREAM

OVERALL MATERIAL BALANCE - LB./HR.

Component	Absorber Vent Gas	Scrubber Vent Gas	Liquid to Scrubber	Liquid from Scrubber
Formaldehyde	7.4	0.4		7.0
Methanol	30.6	0.9		29.7
Hydrogen	123	123		
Carbon Dioxide	558	558		
Carbon Monoxide	64	64		
Oxygen	38	38		
Nitrogen	7147	7147		
Water	178	178	12,500	12,500
Total	8146.0	8109.3	12,500	12,536.7



(b) Condenser

One respondent (14-8) reports a condenser on the scrubber jet. It is not known if this is on the suction or effluent because of incomplete data. It has been included in Table FS-7.

2. Feasible Devices Not Currently Employed

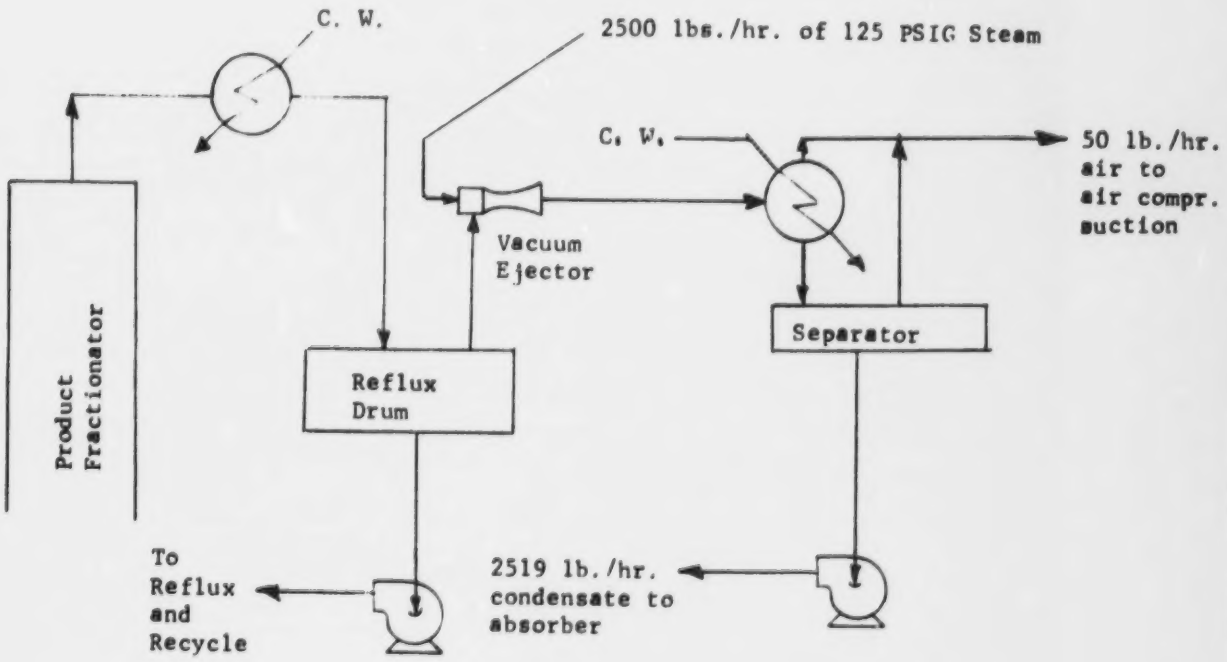
Total Recycle System

Table FS-11 presents a material balance and a rudimentary flow diagram for a total recycle system that will recover all emissions from the subject source. The primary disadvantage of this scheme is the possibility that trace impurities might tend to concentrate in the system. Further study appears to be warranted to determine if such a build-up occurs, and whether or not it can be controlled with a small purge.

TABLE FS-11
TOTAL RECYCLE SYSTEM
FOR
100 MM LB./YR. FORMALDEHYDE PLANT
FRACTIONATOR VENT GAS

OVERALL MATERIAL BALANCE - LB./HR.

Component	Fractionator Vent Gas	Steam to Ejector	Ejector Discharge	Gas to Compressor	Condensate to Absorber
Formaldehyde	4		4		4
Methanol	10		10		10
Air	50		50	50	
Water	5	2500	2505		2505
Total	69	2500	2569	50	2519



V. National Emissions Inventory

Based upon the emission factors shown in Table FS-5, the total approximate emissions from existing silver process formaldehyde plants are as follows:

Component	Average Emissions (a) Lb./Lb. of 37% Formaldehyde	Total Emissions (b) MM Lbs./Year
Hydrocarbons	.0040	23.7
CO	.0180	106.5
	.0220	130.2

Since formaldehyde production has been reported as undergoing no seasonal variation, emissions should be fairly constant throughout the year; unless absorber tower top tray cooling capacity is marginal (or does not exist). In that case, emissions will tend to be somewhat higher during warm weather.

(a) Weighted average based on individual plant emission factors and formladehyde production.

(b) Based on 5914 MM lbs./year silver process capacity and assuming production rate equals capacity.

VI. Ground Level Air Quality Determination

A summary of air emissions data from the various surveyed formaldehyde plants has been presented in Table FS-5. This table includes emissions from absorber vent streams and fractionator ejector discharge plus the emissions from various start-up vents.

Table FS-5 provides operating conditions and physical dimensions of the various vent stacks. The EPA will use this information together with the air emission data to calculate ground level concentration for use in subsequent reports.

VII. Cost Effectiveness of Controls

Table FS-12 presents a cost analysis for alternate methods of reducing air pollution from the various vents. Economic data presented in this table are for a new plant producing 100 MM lbs./year of 37% formaldehyde and are based on the following:

A. Investment (1973 Dollars)

1. Incinerators

Published data [14] were used to determine both thermal and catalytic incinerator costs. It should be noted that these costs are considerably lower than reported by respondent 14-10 (see Table FS-7) for his thermal incinerator. The probable explanation lies in the fact that the published data are for "off-the-shelf" units, while the reported plant unit was specially designed for the service.

2. Scrubbers

Investment data provided in questionnaire responses on both the subject process and other processes were used to determine scrubber costs.

3. Others

Investment and installation costs for the various packaged units are estimated values based on previous experience in plant construction. A major portion of this cost represents construction labor.

B. Operating Expenses (1973 Dollars)

1. Depreciation - 10 year straight line.

2. Interest - 6% on total capital.

3. Maintenance - If plant survey data were not provided, maintenance was set at 2% of investment, except for catalytic incinerators, for which the maintenance was set at 4% of investment.

4. Labor - Virtually no operating labor is required for any of the devices listed in Table FS-13. A nominal 8 man hours/week was assumed for the water scrubber and catalytic incinerator and 4 man hours/week labor was assigned to the other devices.

5. Utilities - Unit costs are based on typical value for the Gulf Coast area.

The criteria for functional adequacy of emission control devices cannot be fully established until the pertinent industry regulations are promulgated. Never-the-less, a water scrubbing device (see Table FS-12) would appear to offer acceptable emission control for a modest price, unless carbon monoxide emission regulations are particularly stringent. Consideration must also be given to the fact that the scrubber transfers pollutants from air to water, whereas combustion devices 'destroy' most pollutants.

TABLE FS-12

COST EFFECTIVENESS FOR ALTERNATE (h)

EMISSION CONTROL DEVICES

BASED ON 100 MM LB./YR. FORMALDEHYDE PRODUCTION

Stream	Absorber Vent Gas				
Type of Emission Control Device	Water Scrubber	Thermal Incinerator	Catalytic Incinerator	Plume Burner	Boiler House Vent Gas Burner
Number of Units	1	1	1	1	?
Capacity of each unit - ?	100	100	100	100	?
Feed					
Total Flow, Lb./Hr.			8146		
SCFM			2170		
Composition, Ton/Ton HCHO (37%)					
Hydrocarbons			.0031		
Particulates			0		
NO_x			0		
SO_x			0		
Carbon Monoxide			.0052		
Combined Effluent					
Total Flow, Lbs./Hr.	8109	15132	22979		~15,000
SCFM	2163	3515	5244	>2200	~ 3,500
Composition, Ton/Ton HCHO (37%)					
Hydrocarbons	.0001	0	0	.0003	0
Particulates	0	0	0		0
NO_x	0	(d)	(d)	(d)	(d)
SO_x	0	0	0		0
Carbon Monoxide	.0052	0*	0*	.0005*	0*
Emissions Control Efficiency (i)					
SE (%)	96.6				
CCR (%)		100	100	90	100
SERR (%)	94.6	99+	99+	89+	99+
Investment, $	(a,g)	(b)	(b)	(c)	(a)
Purchased Cost	12,900	23,000	24,000	14,000	
Installation	9,700	23,000	19,000	14,000	
Total Capital	22,600	46,000	43,000	28,000	44,000
Operating Cost, $/Yr.	(a,g)	(b)	(b)		
Depreciation (10 years)	2,300	4,600	4,300	2,800	4,400
Interest on Capital (6%)	1,400	2,800	2,600	1,700	2,600
Maintenance	1,400	900 (2%)	1,700 (4%)	600 (2%)	900 (2%)
Labor, @ $4.85/hr.	2,000	1,000	2,000	1,000	1,000
Utilities					
Power, 1c/KWH		300	300		1,000
Fuel, 40c/MM BTU		500	400	700 (c)	-13,000
Process Water 10c/M. Gal.					
Total Utilities	1,100	800	700	700	-12,000
Catalyst			2,800		
Total Operating Cost, $/Yr.	8,200	10,100	14,100	6,800	-3,100

(a) Based on cost provided by formaldehyde producer on similar installation.

(b) ex afterburner systems study by Shell Development Co. for EPA (Contract EHSD 71-3).

(c) Based on flare costs for special study. Includes minimum fuel estimated to sustain flame at all times.

(d) Only from atmospheric nitrogen.

Shee Sheet #2 for additional notes.

TABLE FS-12
COST EFFECTIVENESS FOR ALTERNATE (h)
EMISSION CONTROL DEVICES
BASED ON 100 MM LB./YR. FORMALDEHYDE PRODUCTION

Stream	FRACTIONATOR VENT GAS	
Type of Emission Control Device	Total Recycle System	Scrubber
Number of Units	1	1
Capacity of Each Unit, %	100	100
Feed		
Total Flow, Lb./Hr.	2569	
SCFM	894	
Composition, Ton/Ton HCHO (37%)		
Hydrocarbons	.0011	
Particulates	0	
NO_x	0	
SO_x	0	
Carbon Monoxide	0	
Combined Effluent		
Total Flow, Lbs./Hr.	Not Applicable	56
SCFM	No Emissions	
Composition, Ton/Ton HCHO (37%)		
Hydrocarbons		.00007
Particulates		0
NO_x		0
SO_x		0
Carbon Monoxide		0
Emissions Control Efficiency (i)		
SE - %	100	94
CCR - %	100	94
SERR - %	(f,g)	(f,g)
Investment - $		
Purchased Cost	5500	>5500
Installation	(f,g)	(f,g)
Total Capital		
Operating Cost, $/Yr.		
Depreciation (10 years)	600	
Interest on Capital (6%)	300	
Maintenance	100 (2%)	
Labor, @ $4.85/Hr.	1000	
Utilities		
Power, 1c/KWH		
Fuel, 40c/MM BTU		
Process Water 10c/M. Gal.		
Total Utilities	100	
Catalyst		
Total Operating Cost - $/Yr.	2100	>2100

(f) These units are so small that estimates of investment and cost are subject to more than normal error.
> Excludes water treatment cost.

(h) 1973 dollars.
(i) See Appendix for explanation.

Thermal incineration of the absorber vent gas stream offers the most effective means of controlling emissions. Operating costs are higher than for a scrubbing device, but only because depreciation and interest on the more expensive incinerator are higher. Although the caloric content of the absorber vent gas is high enough to sustain combustion, a nominal amount of fuel will be required (as indicated by plant survey data) for pilots and device start-up. Unfortunately, the caloric content of this stream is not high enough to justify the coupling of a waste heat boiler with the incinerator. A thermal incinerator could be incorporated with either existing or new plants.

The installed cost of a catalytic incinerator (excluding catalyst costs, which are considered as operating costs) is slightly less than that of a comparable thermal incinerator. This results primarily from its lower operating temperature, and the effect thereof on fabrication and installation. Increased maintenance and catalyst charges result in operating expenses 40% higher than for non-catalytic incinerators. Emission control capability has been depicted as being comparable to that of thermal devices, although the possibility for catalyst failure through poisoning, etc., always exists.

Supplementing boiler house fuels by burning tail gas in special burners within the boiler fire box has many attractions, not the least of which is a modest credit in operating costs. Cost data on this device - as shown in Table FS-12, have been derived from plant surveys and promotional literature by the prospective licensor. The licensor made claims for better "pay-out" than is shown in Table FS-12, but these could not be corroborated by the (limited) available data. Note also that licensening fees have not been included in the operating costs.

The economic data presented for the various combustion devices are based on processing a typical absorber vent gas having a gross heating value of 62 BTU/SCF. Should the heating value fall much below 62 (as a result of different air/methanol ratios, catalyst selectivity, absorber temperature, etc.) the tail gas could fail to sustain combustion without the addition of supplemental fuel. This would, of course, increase operating costs. Circumstances resulting in increased heating value would affect the economics of only the boiler house burner, which would show a proportionately larger operating credit.

Costs for installing the various absorber vent pollution control equipment in existing plants would, for the most part, be the same or only slightly higher than the figures shown in Table FS-12. The actual cost differential would depend largely on space availability and location relative to associated process equipment. The single exception is the absorber vent gas water scrubber. The Table FS-12 cost data for this unit are based on a "piggy-back" type close-coupled facility. Installation of this type of unit in an existing plant would be impractical. Additionally, a non "piggy-back" type unit would require a vent gas blower to overcome the increased ΔP caused by connecting piping. Thus, investment and operating costs would be higher for installation of this system in an existing plant.

The investment and operating cost for the two devices discussed for control of fractionator vent gas emissions are based primarily on in-house experience with similar equipment. However, the extremely small size of the units involved makes accurate estimation difficult. Both the investment and operating costs for either unit will be minimal.

However, costs for the scrubber will be higher than for the recycle system. Thus, the cheaper system is more efficient and is the preferred method of emission control for this source.

VIII. Source Testing

It is recommended that source sampling should be carried out at one or two of the plants employing absorber vent gas combustion devices. Ideally, two sampling programs would be initiated. The first would include a complete set of samples from either plant 14-6* or plant 14-9*, since both utilize the type of equipment recommended for emission control in the most feasible new plant.

It should be noted that the flue gas from the combustion type control devices used in these plants (14-6 and 14-9) may not be segregated from the flue gases of other burners in the boiler house. Thus, meaningful samples could only be obtained when the other burners were shutdown - this may not be practical.

The second sampling program would involve either plant 14-1 or plant 14-10. However, since the operator of plant 14-10* states that his 'fume abatement' unit "represents the latest technical art", then that unit would seem to be the natural choice. Both the feed gases to the incinerator and the flue gases from the incinerator should be sampled and analyzed. It should be noted that the respondent (14-10) states that the flue gas stack is not readily accessible.

It is recommended that the pertinent streams associated with the only water scrubbing device reported (at plant 14-4) not be sampled because of the age of the device. The respondent states that the scrubber was assembled from second hand components and would not be typical of modern installations.

*It may prove to be expedient to contact the operator of the designated plant to determine whether or not his non-surveyed facilities employ the same type devices-since both respondents operate a number of formaldehyde facilities. Alternate locations may prove to be more convenient to either the operator or the EPA.

IX. Industry Growth Projection

Total annual U.S. formaldehyde production is estimated (3,5) to increase to somewhere around 16 billion pounds per year of 37% solution by 1985. If the silver process maintains its present share of the market it will account for the production of 12.5 billion pounds in 1985, see Figure FS-2.

More than half of all formaldehyde produced is consumed by the construction industry. Urea-formaldehyde resins are used as an adhesive in the manufacture of particle board, and consume 25 percent of formaldehyde production. Phenolic resins are used as an adhesive for plywood and consume about 25 percent of production. Melamine resins are used in decorative laminates (kitchen counters, etc.) and consume about eight percent of total production. Demand in these areas is expected to remain high, as housing starts maintain record levels.

Hexamine (hexamethylene tetramine) has been accounting for about six percent of U.S. formaldehyde production the past few years as a result of the use of large quantities of explosives in the Vietnam War. With the withdrawal of U.S. Forces from that area, it is expected that hexamine consumption will drop sharply.

Pentaerythritol (P.E.) accounts for about seven percent of formaldehyde production. P.E. is used in the manufacture of alkyd resin surface coatings. Consumption is expected to remain fairly steady.

Urea-formaldehyde fertilizers consume about five percent of formaldehyde production. Good growth, up to nine percent per year, is expected for this industry.

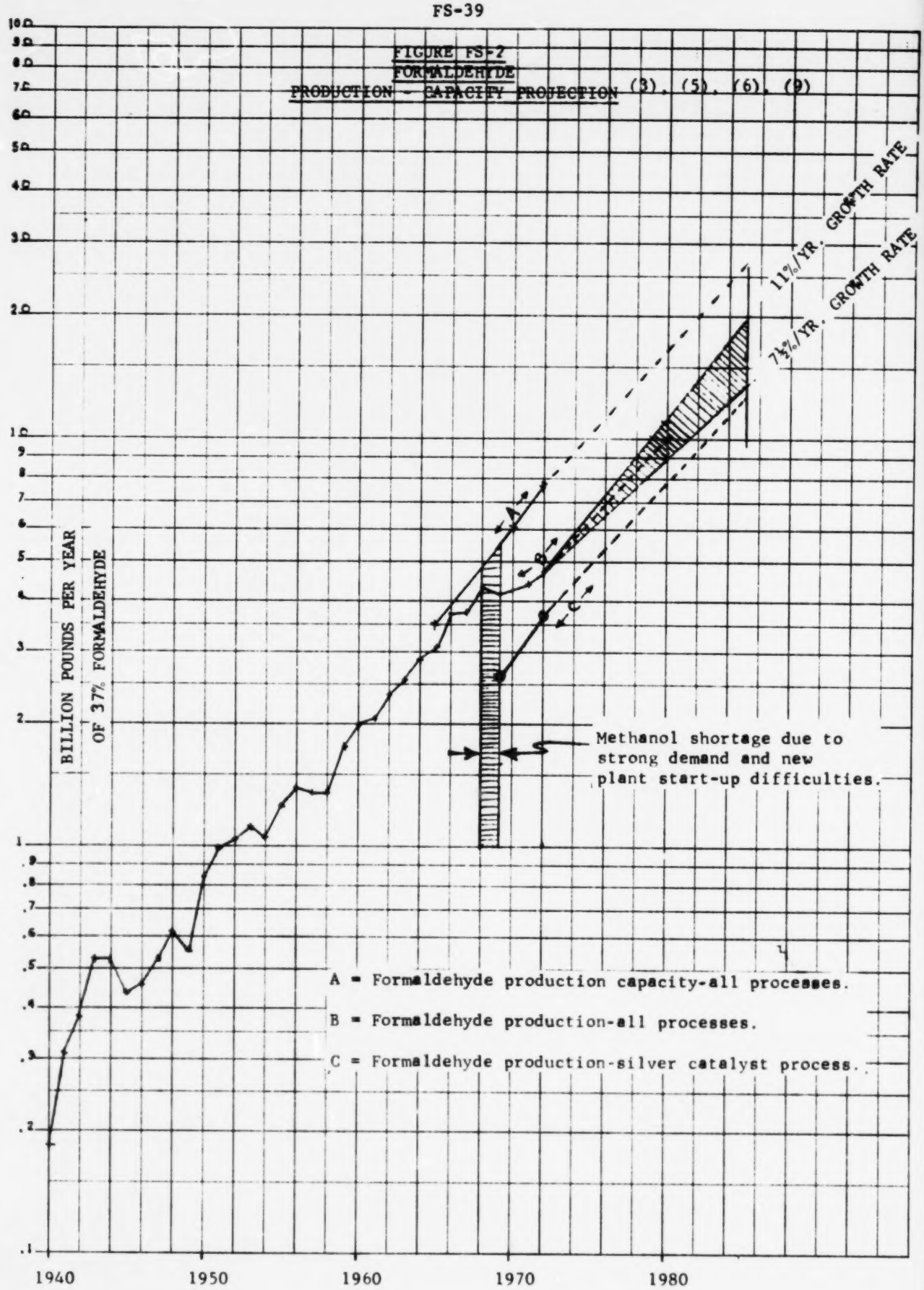
Polyacetal resins account for about eight percent of formaldehyde use. This outlet is expected to maintain a growth rate of 10 percent per year.

Very little formaldehyde is either exported or imported due to the high costs of transporting a water solution. Thus, fluctuations in the general export/import market will not directly affect U.S. formaldehyde production.

The projected increase in formaldehyde production capacity will require the construction of approximately 65 new 100 MM lbs./year silver catalyst process plants between 1972 and 1985. This projection is based on the assumption that the silver process will continue to account for 77 percent of total formaldehyde capacity. It is doubtful that a ressurgence of the partial oxidation or any other third process will develop during this period.

As shown in Table FS-13, methanol costs represents about 50 percent of formaldehyde 'ex works' production costs. Therefore, formaldehyde selling price is greatly influenced by methanol availability. This effect is mitigated to some extent by the fact that the major formaldehyde producers have captive methanol supplies. Methanol prices are currently very low as a result of recent heavy expansions. The long-term outlook for natural gas prices should eventually result in an upturn in methanol prices, but not unitl methanol production catches up to capacity.

FIGURE FS-2
FORMALDEHYDE
PRODUCTION - CAPACITY PROJECTION (3), (5), (6), (9)



X. Plant Inspection Procedures

Plant inspections will be conducted by the appropriate authorities, either on a routine basis or in response to a complaint. The inspecting agent in many cases may have only visual or olifactory observations at his disposal although in some instances, stack monitoring equipment may be available or it might be possible to sample the stack through an accessible sample point.

If the inspector has any reason to suspect that emissions are excessive, some factors that he should consider and/or discuss with plant officials are itemized below:

A. During start-ups, some plants vent reactor feed to the amosphere until the unit is stabilized. Other units vent absorber tail gases to the atmosphere rather than to pollution control devices during this initial on-stream period. A record should be kept as to when and for how long this by-passing occurs. Obviously, an effort should be made to minimize this type of operation. Process economics as well as air pollution considerations dictate that safeguards should be taken to prevent inadvertent opening of the by-pass valves.

B. Proper operation of the absorber column is necessary to limit emissions from the absorber vent gas in plants with no control device on this stream. When the vent gas is discharged directly to the atmosphere the only practical way hydrocarbon emissions can be controlled is by manipulation of top tower temperatures. Many plants refrigerate the top trays for this purpose. Most plants will keep a record of some or all of the following operating variables and their design limits.

   (1) Process and cooling water flow rates and temperatures.

   (2) Formaldehyde and methanol concentration in top tray(s) liquid.

   (3) Temperature and pressure of feed gas.

   (4) Temperature of the (secondary absorber vent gas, especially during warm weather operation.

C. A partially clogged or fouled mist eliminator can result in excessive liquid entrainment.

D. When absorber vent gas is burned, proper operation of the combusting device is essential if emissions are to be minimized. Two types of problems may be expected to be encountered, (1) flame-outs and (2) excessive smoking. Due to the low heating value of the tail gas the first mentioned item is more likely. Plants are likely to periodically record some or all of the following operating variables. Data will also be available on design limits.

   (1) Combustion zone temperature.

   (2) Quantity of excess air (too little will cause smoking, too much can result in flame-outs), which might be indicated by measurements on one or all of the following·

      a. Device draft - inches of water.
      b. Temperature of stack gases.
      c. Air flow rate.

(3) Composition and flow rate of waste gas to the device.

(4) Quantity and heating value of supplemental fuel.

(5) Composition of Stack gases.

E. Periodic visual checks of flare stack opacity may be the only record kept on the operation of this type of device. However, some plants may record the following data for comparison with design limitations.

(1) Feed composition, temperature and flow rate.

(2) Occasional introduction of unusual materials into the flare header.

(3) Plant up-sets causing changes in loading on the flare system or carryover of liquids to the header.

The investigating operative should be cognizant of the fact that seemingly similar plants may have had widely different design criteria, thus the flow, temperature, pressure, composition, etc. characterizing a given stream in one plant cannot necessarily be used as a basis for estimating like data for the same stream in another plant. Nor can data from similar streams in separate plants be used, in themselves, to estimate the comparative efficiencies of related control equipment.

XI. Financial Impact

Table FS-13 presents economics for formaldehyde manufacture in a typical 100 MM lbs./yr. plant. This plant employs neither incineration nor scrubbing devices, but relies solely on absorber tower temperature manipulation for whatever emission control that is achieved. Two cases are shown; the first for the current listed Gulf Coast methanol price of 12¢/gal., and the second for the Los Angeles area price of 17¢/gal. As would be expected, this results in an appreciable difference in return on investment. However, even the operation with the more expensive feedstock is quite profitable.

Table FS-14 shows estimated economics for producing formaldehyde in a new most feasible plant. This plant provides for burning absorber vent gas in the boiler house plus total recycle of fractionator overhead vapors.

Table FS-14 indicates that total production costs for the new most feasible plant will be only very slightly higher than the costs for existing plants. The estimated difference is + .004¢/lb. of 37% formaldehyde. Return on investment for the new most feasible plant is lower by 0.5 to 0.7 percent. The difference in production costs is based on the assumption that the absorber tail gas has a gross heating value of 62 BTU/SCF, and that it partly supplants fuel having a value of 40¢/MM BTU. Should either value be higher, then manufacturing costs for the new most feasible plant would be proportionately lower. In addition, uncertainties about the recycle system warrant investigation.

Table FS-15 shows that modifying existing plants by adding an absorber tail gas plume burner adds only about .014¢/lb. to the works costs of formaldehyde.

Table FS-16 presents a proforma balance sheet for the following cases:

A. An existing plant - with no scrubbing, incineration or fractionator recycle.

B. Existing with plume burner - which is the same as "A" (above) except that the absorber tail gas is burned in a flare-like device.

C. Most feasible new - this plant burns absorber tail gas in the boiler house and totally recycles fractionator overhead vapors.

It was assumed in developing these asset and liability positions that the formaldehyde selling price would be held constant and the small increase in total production costs would be taken out of the profit margin in order to maintain sales at the same level. Capital requirement for the most feasible new plant is estimated to be about $50,000 higher than for an existing plant of the same capacity - 100 MM lbs./year.

An evaluation of the overall environmental impact of the most feasible method of emission control described in this report is as important as the financial impact. In addition to the obvious benefits of the diminution of atmospheric pollution by hydrocarbons and carbon monoxide, one must consider also the savings of both fuel and water effected by the recommended control system. If all new silver process plants employ the described system, fuel savings (as a result of burning tail gas) of the order of 3×10^{12} BTU/year will be realized. This is equivalent to three billion standard cubic feet per year of natural gas. Also, as a result of recovering and reusing ejector

TABLE FS-13
FORMALDEHYDE MANUFACTURING COST
FOR A TYPICAL
EXISTING 100 MM LB./YR. FACILITY

	¢/Lb.	$/Yr.	¢/Lb.	$/Yr.
DIRECT MANUFACTURING COST				
Raw Materials				
Methanol @ 17¢/gal.	1.136			
@ 12¢/gal.			0.802	
Catalysts & Chemicals	.070		.070	
Labor (2 men/shift @ $4.85/hr.)	.079		.079	
Maintenance (5% of Investment)	.100		.100	
Utilities	.061		.061	
	1.446		1.112	
INDIRECT MANUFACTURING COST				
Plant Overhead (110% of Labor)	.087		.087	
FIXED MANUFACTURING COST				
Depreciation (10 years)	.200		.200	
Insurance & Property Taxes (2.3% of Inv.)	.046		.046	
	.246		.246	
MANUFACTURING COST	1.779		1.445	
GENERAL EXPENSES				
Administration (3% of manuf. cost)	.053		.043	
Sales (1% of manufacturing cost)	.018		.014	
Research (2% of manufacturing cost)	.035		.029	
Finance (6% of investment)	.120		.120	
	.226		.206	
Cost ex works	2.005		1.651	
Delivery	.620		.620	
Total Delivered Cost	2.625	2,625,000	2.271	2,271,000
PRODUCT VALUE				
37% formaldehyde - uninhibited @ 3.5¢/lb. (dlvd)	3.500	3,500,000	3.500	3,500,000
Profit before taxes	.875	875,000	1.229	1,229,000
Profit after 52% tax	.420	420,000	.590	590,000
Cash flow		620,000		790,000
ROI		21.0%		29.5%

TABLE FS-14
FORMALDEHYDE MANUFACTURING COST
FOR A TYPICAL NEW PLANT
WITH BOILER HOUSE INCINERATION
100 MM LB./YR. FACILITY

	¢/Lb.	$/Yr.	¢/Lb.	$/Yr.
DIRECT MANUFACTURING COST				
Raw Materials				
Methanol @ 17¢/gal.	1.136			
@ 12¢/gal.			0.802	
Catalyst & Chemicals	.070		.070	
Labor	.081		.081	
Maintenance	.101		.101	
Net Utilities*	.049		.049	
	1.437		1.103	
INDIRECT MANUFACTURING COST				
Plant Overhead (110% of Labor)	.089		.089	
FIXED MANUFACTURING COST				
Depreciation (10 years)	.205		.205	
Insurance & Property Taxes (2.3% of Inv.)	.049		.049	
	.254		.254	
MANUFACTURING COST	1.780		1.446	
GENERAL EXPENSES				
Administration (3% of manufacturing cost)	.053		.043	
Sales (1% of manufacturing cost)	.018		.014	
Research (2% of manufacturing cost)	.035		.029	
Finance (6% of investment)	.123		.123	
	.229		.209	
Cost ex works	2.009		1.655	
Delivery	.620		.620	
Total Delivered Cost	2.629		2.275	
PRODUCT VALUE				
37% formaldehyde - uninhibited @ 3.5¢/lb. (dlvd)	3.500	3,500,000	3.500	3,500,000
Profit before taxes	.871	871,000	1.225	1,225,000
Profit after 52% tax	.419	419,000	.589	589,000
Cash Flow		624,000		794,000
ROI		20.5%		28.8%
ROI SENSITIVITY				
ROI with double capital charges of Table FS-12		19.6%		27.7%
ROI with double capital and operating charges less half operating credits of Table FS-12		19.4%		27.5%

*Assumes .012¢/lb. credit for boiler house fuel savings via utilization of tail gas as supplemental fuel.

TABLE FS-15
FORMALDEHYDE MANUFACTURING COST
FOR A TYPICAL
PLUME BURNER MODIFICATION TO EXISTING
100 MM LB./YR. FACILITY

	¢/Lb.	$/Yr.	¢/Lb.	$/Yr.
DIRECT MANUFACTURING COST				
Raw Materials				
Methanol @ 17¢/gal.	1.136			
@ 12¢/gal.			0.802	
Catalysts & Chemicals	.070		.070	
Labor	.081		.081	
Maintenance	.101		.101	
Utilities	.062		.062	
	1.450		1.116	
INDIRECT MANUFACTURING COST				
Plant Overhead (110% of Labor)	.089		.089	
FIXED MANUFACTURING COST				
Depreciation (10 years)	.203		.203	
Insurance & Property Taxes (2.3% of inv.)	.048		.048	
	.251		.251	
MANUFACTURING COST	1.790		1.456	
GENERAL EXPENSES				
Administration (3% of manufacturing cost)	.054		.044	
Sales (1% of manufacturing cost)	.108		.015	
Research (2% of manufacturing cost)	.036		.029	
Finance (6% of investment)	.121		.121	
	..229		.209	
Cost ex works	2.019		1.665	
Delivery	.620		.620	
Total Delivered Cost	2.639		2.285	
PRODUCT VALUE				
37% formaldehyde - uninhibited @ 3.5¢/lb. (dlvd)	3.500	3,500,000	3.500	3,500,000
Profit before taxes	.861	861,000	1.215	1,215,000
Profit after 52% tax	.414	414,000	.584	584,000
Cash flow		617,000		687,000
ROI		20.4%		28.8%
ROI SENSITIVITY				
ROI with double capital charges of Table FS-12		20.3%		28.6%
ROI with double capital and operating charges of Table FS-12		20.2%		28.6%

TABLE FS-16
PROFORMA BALANCE SHEET
100 MM LB./YR. FORMALDEHYDE MANUFACTURING FACILITY

	Existing	Existing with Plume Burner	New With Boiler House Incinerator (E)
Current Assets			
Cash (A)	148,300	149,200	148,300
Accounts Receivable (B)	291,700	291,700	291,700
Inventories (C)	200,500	201,900	200,900
Fixed Assets			
Plant	2,000,000	2,028,000	2,049,500
Buildings	50,000	50,000	50,000
Land	25,000	25,000	25,000
Total Assets	2,715,500	2,745,800	2,765,400
Current Liabilities (D)	188,300	188,100	187,700
Equity & Long Term Debt	2,527,200	2,557,700	2,577,700
Total Capital	2,715,500	2,745,800	2,765,400

(A) Based on one month's total manufacturing costs (with methanol @ 17¢/gal.).
(B) Based on one month's sales.
(C) Based on 10 MM lbs. of product valued at total cost (ex works).
(D) Based on one month's total cost (dlvd) less fixed manufacturing and finance costs.
(E) Also includes fractionator vent recycle system.

steam (see Diagram, Table FS-11), water consumption by the industry will decrease by 130 million gallons per year. Admittedly, this is a negligible amount but the effect is directionally desirable.

In order to determine the sensitivity of these pollution control cost estimates, both Tables FS-14 and FS-15 show the effect on ROI if investment or operating costs were to double or if operating credits were to halve. These adjustments all show a variation in R.O.I. of less than one percent. All costs in these tables are based on 1973 estimates.

It should be further noted that the inclusion of a plume burner evaluation for existing plants does not constitute a recommendation for its use. The preferred solution, if possible, would be to use vent gases as a boiler house supplement, even on existing plants. If not possible, some existing plant operators might prefer a water scrubber which will control emissions nearly as well as a plume burner with a slightly lower investment, a slightly higher operating cost and no long term fuel gas demands.

XII. Cost to Industry

In the typical present day plant, as depicted in Table FS-13, very little of the plant investment is directly attributable to the cost of air pollution control. Although almost all plants employ mist eliminators on the secondary absorber vent, most have little additional air pollution control. A few pieces of equipment, used primarily for product recovery, do contribute to emission control. It is difficult to categorize them, however, they include the condenser in the fractionator ejector suction line and the cooling coils in the uppermost trays of the absorber.

As noted in Section XI, the plume burner modification of existing formaldehyde plants results in a minor effect on production costs (plus .014¢ per pound - Of 37% formaldehyde). Therefore, the addition of plume burners to existing plants should not pose a significant economic problem to the industry. The total investment required to add this device to all existing silver process plants would be on the order of $2,000,000. The addition of a plume burner to existing plants might be classified as the "most feasible" emission control, but if possible a boiler house incinerator should be considered because it reduces emissions more effectively, saves energy and would only require about $3,000,000 total investment. On the other hand, water scrubbers would reduce emissions nearly as effectively as the plume burner at a total investment of about $1,500,000.

In the "most feasible new plant" presented in Table FS-14, additional air pollution control equipment represents about 2½ percent of total plant investment. The equipment consists of a boiler house incinerator and a fractionator vent recycle. The resulting total production cost will be an estimated .004¢/lb. higher than for the present day typical unit. Thus, the costs involved should not reduce growth in demand via the requirement for higher formaldehyde prices.

Assuming all new silver process plants built between now and 1980 incorporate these types of air pollution control equipment, the total incremental capital cost will be on the order of $3,000,000.

The projected effect of the above expenditures on future air emissions is shown in Table FS-17 where in:

The first column depicts 1985 emissions for the situation where no pollution control devices (as defined in Section IV) are employed. The total emission rate would be nearly 275 MM lbs./year.

The other three columns show the estimated 1985 emissions from existing plants if they were to be equipped with water scrubbers, boiler house incinerators or plume burners respectively, on the absorber vent gas stream.

These three columns also indicate the total 1985 estimated emissions under these three alternatives if all new plants are equipped with the "most feasible new plant modifications" because emissions from these systems are essentially nil.

TABLE FS-17
ESTIMATED 1985 EMISSIONS
FOR ALTERNATIVE CONTROL SYSTEM

Type of Pollution Control	None	Water Scrubber	Boiler House Incinerator	Plume Burner
Plants Involved	Existing & New	Existing	Existing	Existing
Production Involved (MM Lbs./Year)	12,500	5,914	5,914	5,914
Emissions, Lbs./Lb.				
Hydrocarbon	0.0040	0.0012	0.0009	0.0013
Carbon Monoxide	0.0180	0.0180	0.0	0.0018
Total	0.0220	0.0192	0.0009	0.0031
Emissions, MM Lbs./Year				
Hydrocarbon	50.0	7.1	5.3	7.7
Carbon Monoxide	225.0	106.5	0	10.7
Total	275.0	113.6 (1)	5.3 (1)	18.4 (1)
Weighted Emissions (2)				
Hydrocarbons	4,000	568	425	615
Carbon Monoxide	225	107	0	11
Total	4,225	675 (1)	425 (1)	626 (1)

(1) If all new plants (6,586 MM Lbs./Year capacity) are equipped with boiler house incinerators and fractionator vent recycle systems, the total existing and new 1985 emissions will be as shown. Obviously, the emission factors will be somewhat less than half.

(2) Weighting factors are 80 for hydrocarbons and 1 for carbon monoxide. See Appendix for explanation.

XIII. Emission Control Deficiencies

The control of formaldehyde plant emissions is affected by the following technical considerations:

A. Process Chemistry and Kinetics

Production of formaldehyde by the silver catalyst process involves a combination of dehydrogenation and oxidation reactions. The amount of formaldehyde produced is influenced by air/methanol ratios, converter residence time and operating temperature.

1. Converter Feed

(a) Methanol

Methanol feed must be pure. Impurities in the feed will generally end up as impurities in the product. Formic acid, one of the more common formaldehyde contaminants, can be produced through the use of impure methanol. Ion exchange resins are normally used to remove acidic contaminants from the product. Regeneration of these resins may lead to acid waste stream disposal problems. Therefore, in order to minimize pollution, it is desirable to limit impurities in the feed.

(b) Air

Air provides the oxidizing agent for the oxidation reaction, from which the necessary heat is derived to sustain the endothermic dehydrogenation reaction. Sulfur compounds present in the air, such as SO_2, will poison the silver catalyst and must be removed if the catalyst is to attain an economical cycle life. Prevention of catalyst poisoning is usually accomplished by caustic washing the air, which also removes CO_2.

(c) Air/Methanol Ratio

Because the major portion of the contaminants emitted by a formaldehyde plant are those transported to the atmosphere via the venting of the non-reactive portion of the feed air, lesser amounts of air or lower air/methanol ratios's will decrease those contaminants. However, lower air/methanol ratios will also result in lower methanol conversion and thus overall yield may increase.[1] The economic feasibility of this type of control has not been investigated.

2. Converter Operating Conditions

Converter operating conditions influence methanol conversion rate and to some extent, the amount of non-selective products formed. One of the non-selective products, carbon dioxide, is a major component of the absorber vent gas stream. Converter operating conditions are normally selected to obtain the optimum balance between conversion and selectivity.

3. Catalyst

There are two basic types of catalysts used in the subject process, silver crystal catalyst and silver gauze catalyst. The newer crystal catalyst is reported to give higher yields.[11] It seems reasonable to surmize that the higher yields are achieved through better selectivity, and not merely through increased conversion. If so, the newer catalyst would produce fewer emissions. Additionally, a catalyst with a longer cycle life would require fewer shutdowns and start-ups for regeneration or replacement and thus emissions associated with these activities would be correspondingly lower. Unfortunately, detailed performance comparisons of the various silver catalyst are not readily available.

B. Process Equipment

1. Absorber

The absorber tail gas contains both gases and uncondensed vapors. The uncondensed hydrocarbon vapors (methanol and formaldehyde), because of their high 'weighted' value, constitute the single most significant source of emitted pollutants in the formaldehyde plant. More complete condensation of the hydrocarbons is possible if the absorber pressure is increased or the top temperature is decreased. Unfortunately, neither action is practical. Increasing pressure to a level sufficiently high to significantly affect vapor-liquid equilibria would result in prohibitively high equipment and utility costs. Decreasing the tower top temperature appreciably is impractical because the freezing point of the liquid on the top tray is close to 32° F; which, after allowing for a normal margin of safety, is not significantly lower than the temperature at which many producers actually operate their absorbers.

2. Product Fractionator

The product fractionator is operated at sub-atmospheric pressure. This permits maintainence of the tower bottoms at a temperature sufficiently low to avoid problems with formaldehyde polymerization. Emissions are associated with the operation of the vacuum system.

C. Control Equipment and Operations

The proposed combustion of absorber tail gas and recycling of fractionator vent gas is one method of controlling formaldehyde plant emissions. There are no apparent significant deficiencies in this system, however, refer to Section IV for discussion of this subject.

XIV. Research and Development Goals

If the technological deficiencies discussed in Section XIII are to be overcome, additional R & D is desirable in the following areas:

A. Existing Plants

1. Improved Catalyst

It would be desirable to have a more selective catalyst in order to produce fewer by-products and improve methanol utilization.

Published data [11] state that the newer crystalline catalysts show better yields than the silver gauze catalysts. It is believed that most new plants do utilize the silver crystal catalysts. However, the vent gas composition reported by questionnaire respondents utilizing the silver crystal catalyst indicates that there is still room for improvement. Analyzing catalyst performance via the technique described by Walker [1], one discerns (from questionnaire data) that catalyst selectivity for a typical 100 MM lb./yr. silver crystal plant is of the order of 94%. Improvement beyond that point could best be handled by the process licensors.

B. New Plants

In addition to the above R & D area, which has application to both new and existing plants, the following items would require new facilities for utilization of gained technology:

1. Oxygen Source

A combination of pure oxygen feed in place of air, and recycling of vent gas to the converter could reduce net emissions and improve feed utilization. Additionally, the necessity of caustic scrubbing the air feed would be negated due to the purity of standard merchant oxygen.

The possibility of better feed utilization through improved selectivity is enhanced by the observation that such benefits have been claimed to accrue to tail gas recycling operations in metal oxide process plants. Certainly this would be a prime area for investigation by any R & D program.

2. Tail Gas Combustion

The technology required for the efficient combustion of absorber tail gas has been in existance for some time. However, the technology required for the economic utilization of tail gas as a dependable boiler house fuel supplement is of a higher order. One licensor claims to have perfected this methodology, but it would be desirable to have the performance of the required facilities substantiated by the presentation of detailed economic and technical data.

XV. Research and Development Program

The following proposed project relates to that area of R & D work which seems to offer the best chance for obtaining a method of reducing emissions from future formaldehyde plants:

PROJECT PROPOSAL

1. Title - Reduction of Vent Gas Emissions from the Silver Catalyst Formaldehyde Process via Modifications in the Manufacturing Procedure.

2. Object

To reduce vent gas emissions from the silver catalyst formaldehyde process by modifying the manufacturing procedure.

3. Estimated Project Costs (see Table FS-18 for cost breakdown)

Capital Expenditures	$ 63,900
Operating Costs	
Unit Operation	62,500
Services	11,400
Process Engineering	9,100
Miscellaneous	5,800
Contingency	76,300
	$229,000

4. Scope

This project would seek to reduce emissions in the vent gas from the manufacturing of formaldehyde from methanol by modifying the catalytic process. A small pilot plant would be constructed. This pilot plant would be connected to an on-line gas chromatograph which could sample the total effluent stream and the vent gases. Data from the pilot plant would be used to develop a mathematical model for the process.

5. Program

(a) Construction of Pilot Unit

The first phase in this program would be construction of a small pilot unit. This unit would include a quench system and product absorber to both simulate commerical operations and avoid product decomposition. Effluent gases from the reactor and absorber would be connected to an on-line gas chromatograph.

(b) Process Research

A number of process modifications will be explored to determine their effect on methanol conversion, selectivity to formaldehyde, and emissions in the vent gas. One of these modifications will be substitution of oxygen for air in the feed. In the beginning a standard silver catalyst will be used. However, large changes in process conditions may require modifications in the catalyst.

(c) Process Engineering

Date from the process research will be used to develop a model

TABLE FS-18
DETAILED COSTS
FOR
R & D PROJECT

A. Capital Expenditures		
Test Unit Construction		$ 60,000
Unit Checkout		
Professional, 2 weeks		1,800
Operator, 4 weeks		2,100
	Total	63,900
B. Operating Expenses		
Unit Operation		
Professional, 40 weeks		36,500
Operator, 50 weeks		26,000
Services		
Computer Operator, 5 hrs./week x 50 weeks		3,200
Analytical, 5 weeks		3,200
Unit Maintenance, 1 day/week x 50 weeks		4,500
Physical and Catalyst Testing, 1 week		500
	Total	73,900
C. Process Engineering		
Professional, 10 weeks		9,100
	Total	9,100
D. Miscellaneous		
Computer Time		2,000
Materials		2,000
Report Writing, Professional, 2 weeks		1,800
	Total	5,800
E. Totals		
Total of A through D		152,700
Contingency, 50%		76,300
Total Cost		$229,000

for methanol oxidation to formaldehyde. This model will define optimum conversions and selectivities as a function of vent gas emissions.

6. Timetable

It is estimated that the above program will require a total of 17 months to complete.

XVI. Summary of Analytical Methods for Formaldehyde Plant Stack Emissions

1. Methods in Use

A total of fourteen plants were surveyed to obtain information on emission measurement techniques, see Table FS-19 for summary. Of these, four have performed no stack gas analyses and an additional four have performed only Orsat analysis of the absorber vent gases to determine inorganic constituents. Plant number 14-15 has performed "volumetric" analyses for formaldehyde and methanol in addition to Orsat measurement, but no details could be obtained on the actual procedure.

Plant number 14-1 uses a combination of Orsat analysis along with a sodium sulfite analysis for formaldehyde and chromic acid for methanol. Plant 14-3 uses the same sodium sulfite analysis for formaldehyde, but a Fisher gas partioner for inorganic gases and a gas chromatographic technique for methanol. The sodium sulfite and chromic acid procedures are referenced (1), but the details of the remaining methods are unknown.

Comprehensive analysis of absorber vent gases is performed at plant 14-8 by a combination of chromatographic and wet chemistry procedures. A sample is drawn by vacuum through a train consisting of two batch scrubbers, two 500 ml. glass bulbs and a wet test meter. The flow rate is maintained to obtain a sample of approximately three cubic feet over a one and one-half hour period. The scrubbers are filled with distilled water and placed in an ice bath so as to promote condensation/absorption.

The scrubber liquid is weighted and an aliquot taken for methanol analysis using an Aerograph Model 600 gas chromatograph. A 1/8" x 10' aluminum column packed with Porepak Q is combined with a hydrogen flame ionization detector. Column temperature is maintained at 80° C. Carrier gas is nitrogen at a flow rate of 35 ml per minute and the hydrogen flow is 27 ml per minute. An injection port temperature of 150° C is maintained. Calibration is maintained by the sequential injection of 1 ml of sample followed by 1 ml of a mixture of 100 ml sample spiked with 1 ml of reagent methanol.

The unused portion of the scrubber solution is analyzed for formaldehyde using a modification of the Walker sodium sulfite method (1) intended to eliminate interference by CO_2 in the sample. The modification consists of adjusting the pH of both sample and sodium sulfite solutions to the end point of thymophthalein prior to mixing and analysis.

Non-condensable gases from the bulb samplers are analyzed using a Loenco thermal conductivity gas chromatograph with three columns. Hydrogen and oxygen are run on a 1/4" x 7' aluminum column containing 5A molecular sieve of 30-42 mesh size. The carrier gas is argon at a column pressure of 10 PSIG, ambient temperature, detector current of 55 ma an d reverse polarity. A 1 ml gas sample is used. Nitrogen and carbon monoxide are measured using a 1/4" x 15' aluminum column packed with 13x molecular sieve of 30-42 mesh size. Operating parameters include: helium carrier gas; ambient temperature; 150 ma detector current and 3 ml sample size. Carbon dioxide is determined using a 3/16" x 20' aluminum column packed with 12.5 percent hexamethylphosphoramide and 7.5 percent tributylphosphate on 60-80 mesh Chromosorb P. Operating conditions include: helium carrier gas at 30 ml/minute, ambient temperature, 150 ma detector current and 3 ml gas sample size.

TABLE FS-19
SUMMARY OF
SAMPLING AND ANALYTICAL METHODS

PLANT	COMPONENT	METHOD	BASE	MODEL	COLUMN LENGTH FEET	COLUMN DIAMETER INCHES	CARRIER GAS	CARRIER GAS RATE ML MIN	DETECTION UNIT TYPE	COLUMN PACKING	ABSORBENT	COLUMN TEMP °C	COLUMN PRESS PSIG
14.1	CO_2 CO H_2 N_2 HCHO CH_3OH	BURRELL SODIUM SULFITE (WALKER) CHROMIC ACID (WALKER)											
14.3	CO_2 CO H_2 O_2 HCHO CH_3OH	GAS PARTITIONER SODIUM SULFITE (WALKER) CHROMATOGRAPH	FISHER F & M	700	8 '	1/8	HELIUM ARGON			#1 PPG #2 13X MOL SIEVE CARBOWAX 1000		- 50	
14.4	ALL	EQUILIBRIUM CALC.											
14.6	ALL	ORSAT											
14.7	ALL	EX DESIGN CALC.											
14.8	H_2 O_2	CHROMATOGRAPH	LDENCO		7	1/4	ARGON		THERMAL CONDUCTIVITY	5A MOL SIEVE		AMBIENT	10
	N_2 CO	CHROMATOGRAPH	LDENCO		15	1/4	HELIUM	30	THERMAL CONDUCTIVITY	13X MOL SIEVE		AMBIENT	
	CO_2	CHROMATOGRAPH	LDENCO		20	3/16	HELIUM	30	THERMAL CONDUCTIVITY	CHROMOSORB P	12.5% HEXAETHYL PHOSPHORAMIDE	AMBIENT	
	HCHO CH_3OH	SODIUM SULFITE (WALKER) CHROMATOGRAPH	AEROGRAPH	630	10	1/8	NITROGEN	35	H_2 FLAME IONIZATION	PORAPAK Q	7.5% TRIBUTYL PHOSPHATE	AMBIENT -80	
14.9	ALL	ORSAT											
14.11	H_2 N_2 O_2 CO	CHROMATOGRAPH	VARIAN	1700	15	3/16	HELIUM	30	THERMAL CONDUCTIVITY	PORAPAK Q		80	
	CO_2	CHROMATOGRAPH	VARIAN	1100	15	3/16	HELIUM	30	THERMAL CONDUCTIVITY	PORAPAK Q		-85	
	CH_4 CH_3OH METHYLAL METHYL FORMATE DIMETHYL ETHER METHOXY METHYLAL	CHROMATOGRAPH	PERKIN ELMER	154	20	1/8	NITROGEN	30	THERMAL CONDUCTIVITY	DNCS CHROMOSORB W	20% 1,2,3 TRIS (2 CYANOETHOXY) PROPANE	-100	
14.10	ALL	NOT AVAILABLE											
14.12	ALL	ORSAT											
14.14	ALL	EX DESIGN CALC.											
14.15	H_2 N_2 O_2 CO CO_2 CH_3OH, HCHO	ORSAT "VOLUMETRIC"											
14.18	ALL	ORSAT											
14.20	ALL	EX DESIGN CALC.											

At plant 14-11, chromatographic techniques are used for complete inorganic and organic gas analysis. Hydrogen, nitrogen, oxygen and carbon monoxide are measured on a Varian Model 1700 thermal conductivity instrument. A 3/16" x 15' aluminum column containing 50-80 mesh Porepak Q is operated at 60° C using 30 ml/minute of helium carrier gas. For carbon dioxide analysis, the column temperature is elevated to +65° C.

Organic absorber vent gas constituents analyzed include methane, methanol, methylal, methyl formate, dimethyl ether, methoxymethylal. A Perkin-Elmer Model 154 chromatograph with 1/8" x 20' aluminum column and thermal conductivity detector is used. Column packing consists of 20 percent 1,2,3 tris (cyanomethoxy) propane on 60-80 mesh Chromosorb W. Nitrogen carrier gas at 30 ml/minute is used along with a column temperature of 100° C.

2. Discussion

As may be noted from the previous section, stack gas analysis other than the Orsat-type is the exception rather than the rule in the formaldehyde industry. Even where organic constituents are measured, the frequency is low. Hoever, from the standpoint of analytical technology, adequate methods are available and are in use in several plants. The sulfite and chromic acid methods (1) are simple and inexpensive to perform and are acceptable for routine emissions monitoring. Through gas chromatography, complete organic analyses are practical on either a grab or continuous sample basis. No centralized effort is felt to be warranted for further methods development.

XVII. Emergency Action Plan for Air Pollution Episodes

A. Types of Episodes

The alleviation of Air Pollution Episodes as suggested by the U.S. Environmental Portection Agency is based on a pre-planned episode emission reduction scheme. The criteria that set this scheme into motion are:

1. Alert Status - The alert level is that concentration of pollutants at which short-term health effects can be expected to occur.

2. Warning Status - The warning level indicates that air quality is continuing to deteriorate and that additional abatement actions are necessary.

3. Emergency Status - The emergency level is that level at which a substantial endangerment to human health can be expected. These criteria are absolute in the sense that they represent a level of pollution that must not be allowed to occur.

B. Sources of Emissions

As outlined in the foregoing in-depth study of "Formaldehyde Manufacture by the Silver Catalyst Process" there are two continuous and three intermittent vent streams to the atmosphere.

1. Continuous Streams

   (a) Absorber Vent - The emissions from this source represent by far the largest and most important atmospheric emission associated with this process. The stream consists of reaction by-products and varies in composition with catalyst age or activity.

   Except for a mist eliminator in the top of the secondary absorber, most plants do not employ emission control devices on the absorber vent. Those that do, usually utilize some type of combustion system.

   (b) Product Fractionator Vent - Reports indicate that the product fractionators are usually operated at sub-atmospheric pressures by using steam ejectors or vacuum pumps. The gaseous effluent from this system is continuous in nature with little change in composition provided tower operating conditions (pressure, temperature and reflux) are maintained at the normal operating levels.

2. Intermittent Air Emissions

   (a) Converter Start-Up Vent - This stream represents the converter feed during start-up and is usually vented to the atmosphere until stabilized conditions are obtained. It is then gradually introduced to the converter for processing. The vent time is reported to be 30 minutes per converter start-up. Another type of start-up vent is employed when the absorber vent stream is burned in a combustion device. In this case, the absorber vent stream is directed to the atmosphere until stabilized then it is routed to the incinerating device.

(b) Converter Emergency Vent - This vent is presumed to be an explosion type of quick opening valve or bursting disc that would operate only in event of sudden high pressure. Such an occasion would be very infrequent and insignificant as an emission source since flow would be of a short duration (1-2 minutes).

C. Abatement Techniques

As the various levels of the pre-planned episode reduction scheme are declared (Alert, Warning and Emergency) a progressive reduction in the amount of air pollutants emitted must be made. This could ultimately lead to total curtailment of pollutant emissions if the emergency level becomes imminent.

The extent of the required cutback in emissions from formaldehyde plants will be at the jurisdiction of the environmental governing agency. It will depend on the relative amount of offending constituents contributed by formaldehyde production to the overall emissions which resulted in the pollution episode. This plus other factors will be used by the control authorities in determining the amount of emissions to be tolerated during various episodes.

Formaldehyde manufacturing facilities by the Silver Catalyst Process generally consist of one or more converters with a common set of absorbers (2) and a product fractionator. In plants with multiple converters in a producting train of equipment, a certain degree of flexibility for a partial reduction in air pollutant emissions is usually possible by shutting down one or more converters. There is, in addition, the option of maintaining operation of all converters and to "turndown" the plant capacity for the required reduction. In the first instance if one or more catalytic converters are taken out of service, a rebalance of flows through the equipment is required. The polluting constituents, if they were discharged directly to the atmosphere would be reduced by the percentage which the air flow is reduced. In the second instance a "turndown" of plant capacity would produce the same type of results. In both cases conversion efficiency must be maintained.

In either of the options presented above for a partial reduction in atmospheric pollutants, consideration must be given to the actual emission into the atmosphere. For example, in plants that employ combustion devices the reduction in plant capacity, whether by shutting down a converter or turndown in capacity by reducing feed, would decrease the amount of combustibles flowing to the incinerating devices. If the air rate is not cut back proportionally, this could make it necessary to add supplemental fuel to replace these combustibles in order to prevent burner flame out. In the event the emissions are used in a steam generating unit, supplementary fuel may also be required to maintain the steam balance.

Two to four hours will be required to affect a partial reduction in plant capacity with a similar period for return to normal operating levels.

Product fractionator vacuum producing equipment will remain in service during the partial reduction. The sole requirement is for the maintenance of satisfactory operating conditions on the tower.

The converter start-up vent should not be required during an alert condition. If a "turndown" in capacity is used to reduce emissions during an episode, converter venting will not be required upon resumption to normal formaldehyde production levels. However, this vent is necessary if individual converters are shutdown.

The same applies to the absorber vent in plants that use combustion control devices. In these units, the vent would be used only in the event the entire train of equipment was starting up.

The converter emergency vent will presumably not be a source of emissions during the alert condition. As the name implies, it would emit pollutants only during an emergency. In this case, it is presumed that the entire plant would be shutdown.

1. Declaration of Alert Condition - When an alert condition is declared, the episode emission reduction plan is immediately set into motion. Under this plan in addition to notifying the manufacture of the alert condition, it may be deemed necessary by the governing environmental protection agency to somewhat reduce emissions from formaldehyde manufacture in order to prevent further increases in pollution level which could result in warning or emergency episodes. This reduction would be accomplished by employing one of the foregoing options. This will reduce the principal source of emission, represented by the absorber vent, to a value approximately equivalent to the reduction made in formaldehyde production. Usually the alert condition can be expected to continue for 12 hours or more.

2. Declaration of Warning Condition - When the air pollution warning episode is announced a substantial reduction of air contaminants is desirable even to the point of assuming reasonable economic hardship in the cutback of production and allied operations. This could involve a 50-60 percent decrease in formaldehyde production.

3. Emergency Condition - When it appears that an air pollution emergency episode is imminent, all air contaminants may have to be eliminated immediately by ceasing production and allied operations to the extent possible without causing injury to persons or damage to equipment.

   The cessation of operation of the producing units whether wholly or in part will not result in increased emissions. Start-up operations, however, will produce air pollutant emissions for short periods as previously outlined.

D. Economic Considerations

The economic impact on formaldehyde manufacturers of curtailing operations during any of the air pollution episodes is based on the duration and number of episodes in a given period. It is indicated that the normal duration of air pollution episodes is usually one to seven days with meteorology episode potentials as high as 80 per year.[17] The frequency of air pollution episodes in any given area is indicated as being one to four per year. These data do not differentiate between the episode levels. Normally since the alert level does not require a

cutback in production, it will not influence plant economics. Therefore, in discussing economic considerations resulting from the air pollution abatement plant, it is necessary to estimate the frequency and number of warning and emergency episodes. For the economic study, it has been assumed that three warning and no emergency episodes occur per year. Each warning episode is assumed to require a 50 percent reduction in air contaminants for a period of 5½ days. This then equates to a complete loss in plant production of about 8½ days per year.

The financial impact resulting from this loss in production is shown in Table FS-20. This table contains comparative manufacturing costs for an existing 100 MM Lbs./Year facility without extensive pollution control (Table FS-13) and for a most feasible new facility of the same capacity (Table FS-14). Economics are shown for each of these plants with methanol feed at 12 and 17 cents per gallon with and without the financial impact accredited to the air pollution episodes. It should be noted that whereas the proposed cutback in formaldehyde production for emission control appears small (2.5 percent on a yearly basis) it has a substantial influence on net profit (4.0 percent to 5.0 percent reduction) on the cases presented.

E. Summary of Estimated Emissions

In the foregoing it has been implied that a reduction in air pollutant emissions is necessary for the various air pollution levels that may be encountered. This was primarily predicated on existing plants which do not have the most sophisticated pollution control equipment. However, special consideration should be made in the EAP for Air Pollution Episode Avoidance for new and existing plants that employ incineration control equipment on the absorber vent. The following presents estimated air emissions for a typical present day system without incineration and the most feasible new plant with this type of control plus recycle of fractionator vent gas.

Pollutant	Typical Present Day System, Lb./Lb. of 37% Formaldehyde	Most Feasible New Lb./Lb. of 37% Formaldehyde
Hydrocarbons	0.0040	0
Carbon Monoxide	0.0180	0
Total	0.0220	0

As noted in the above, total emission of hydrocarbon and carbon monoxide has been reduced to zero levels on the most feasible new plant. However, it can be expected that some quantity of NOx will be made in the incinerator. Despite this, one respondent reported that the normal process emissions from his plant contained only oxygen, nitrogen, carbon dioxide and uncombined water. In this particular case and on similar facilities that can demonstrate the absence of polluting constituents in their atmospheric emissions no steps would need to be taken during any of the air pollution episodes.

The particular type and conenntration of pollutants in the atmosphere at the time of the episode would dictate the degree to which a reduction would be made on the most feasible new plant. If NOx is the offending material, then a reduction in plant production should be made as outlined

TABLE FS-20
FINANCIAL IMPACT OF AIR POLLUTION EPISODES
ON MANUFACTURING COSTS
FOR 100 MM LBS./YEAR FORMALDEHYDE MANUFACTURING FACILITY
(SILVER CATALYST PROCESS)

	TYPICAL EXISTING PLANT (TABLE FS-13)				MOST FEASIBLE NEW PLANT (TABLE FS-14)			
	Methanol @ 17¢/Gal.		Methanol @ 12¢/Gal.		Methanol @ 17¢/Gal.		Methanol @ 12¢/Gal.	
	No Cut-back In Production	Assuming 8.5 Days Lost Production	No Cut-back In Production	Assuming 8.5 Days Lost Production	No Cut-back In Production	Assuming 8.5 Days Lost Production	No Cut-back In Production	Assuming 8.5 Days Lost Production
Direct Manufacturing Cost, M $/Yr.								
Raw Material								
Methanol @ 17¢/Gal.	1,135	1,108			1,136	1,108		
@ 12¢/Gal.			802	782			802	782
Catalyst and Chemicals	70	68	70	68	70	68	70	68
Labor	79	79	79	79	81	81	81	81
Maintenance	100	100	100	100	101	101	101	101
Utilities*	61	59	61	59	49	48	49	48
Indirect Manufacturing Costs, M $/Yr.								
Plant Overhead	87	87	87	87	89	89	89	89
Fixed Manufacturing Costs, M $/Yr.								
Depreciation, Insurance & Prop. Taxes	246	246	246	246	254	254	254	254

*One formaldehyde manufacturer has commented that these utility charges are low relative to the mixed oxide catalyst process utilities.

TABLE FS-20
FINANCIAL IMPACT OF AIR POLLUTION EPISODES
ON MANUFACTURING COSTS
FOR 100 MM LBS./YEAR FORMALDEHYDE MANUFACTURING FACILITY
(SILVER CATALYST PROCESS)

	TYPICAL EXISTING PLANT (TABLE FS-13)				MOST FEASIBLE NEW PLANT (TABLE FS-14)			
	Methanol @ 17¢/Gal.		Methanol @ 12¢/Gal.		Methanol @ 17¢/Gal.		Methanol @ 12¢/Gal.	
	No Cut-back In Production	Assuming 8.5 Days Lost Production	No Cut-back In Production	Assuming 8.5 Days Lost Production	No Cut-back In Production	Assuming 8.5 Days Lost Production	No Cut-back In Production	Assuming 8.5 Days Lost Production
Manufacturing Costs, M $/Yr.	1,779	1,747	1,445	1,421	1,780	1,749	1,446	1,423
General Expenses								
Administration, Sales, Res. & Finance	226	226	206	206	229	229	209	209
Cost Ex Works	2,005	1,973	1,651	1,627	2,009	1,978	1,655	1,632
Delivery	620	605	620	605	620	605	620	605
Total Delivered Cost	2,625	2,578	2,271	2,232	2,629	2,583	2,275	2,237
Product Value, M $/Yr.								
37% Formaldehyde Uninhibited @ 3.5¢/Lb. (Dlvd.)	3,500	3,413	3,500	3,413	3,500	3,413	3,500	3,413
Profit Before Taxes	875	835	1,229	1,181	871	830	1,225	1,176
Profit After 52% Tax	420	401	590	567	419	399	589	565
Cash Flow	620	601	790	767	624	604	794	770
ROI	21.0%	20.1%	29.5%	28.3%	20.5%	19.5%	28.8%	27.6%

under "Declaration of Warning Status". In this case, NOx would be reduced in proportion to the cutback in production and probably to a greater percentage because of longer residence time and reduced operating temperature of the incinerating device.

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APPENDIX I

BASIS OF THE STUDY

I. Industry Survey

The study which led to this document was undertaken to obtain information about selected production processes that are practiced in the Petrochemical Industry. The objective of the study was to provide data for the EPA to use in the fulfillment of their obligations under the Clean Air Amendments of 1970.

The information obtained during the study includes industry descriptions, air emission control problems, sources of air emissions, statistics on quantities and types of emissions and descriptions of emission control devices currently in use. The principal source for these data was an Industry Questionnaire but it was supplemented by plant visits, literature searches, in-house background knowledge and direct support from the Manufacturing Chemists Association.

More than 200 petrochemicals are currently produced in the United States, and many of these by two or more different processes. It was obvious that the most immediate need was to study the largest tonnage, fastest growth processes that produce the most pollution. Consequently, the following 32 chemicals (as produced by a total of 41 different processes) were selected for study:

Acetaldehyde (two processes)
Acetic Acid (three processes)
Acetic Anhydride
Acrylonitrile
Adipic Acid
Adiponitrile (two processes)
Carbon Black
Carbon Disulfide
Cyclohexanone
Ethylene
Ethylene Dichloride (two processes)
Ethylene Oxide (two processes)
Formaldehyde (two processes)
Glycerol
Hydrogen Cyanide
Maleic Anhydride
Nylon 6
Nylon 6,6
"Oxo" Alcohols and Aldehydes
Phenol
Phthalic Anhydride (two processes)
Polyethylene (high density)
Polyethylene (low density)
Polypropylene
Polystyrene
Polyvinyl Chloride
Styrene
Styrene - Butadiene Rubber
Terephthalic Acid (1)
Toluene Di-isocyanate (2)
Vinyl Acetate (two processes)
Vinyl Chloride

(1) Includes dimethyl terephthalate.
(2) Includes methylenediphenyl and polymethylene polyphenyl isocyanates.

The Industry Questionnaire, which was used as the main source of information, was the result of cooperative efforts between the EPA, Air Products and the EPA's Industry Advisory Committee. After receiving approval from the Office of Management and Budget, the questionnaire was sent to selected producers of most of the chemicals listed above. The data obtained from the returned questionnaires formed the basis for what have been named "Survey Reports". These have been separately published in four volumes, numbered EPA-450/3-73-005a, b, c, and d and entitled "Survey Reports on Atmospheric Emissions from the Petrochemical Industry - Volumes I, II, III, and IV.

The purpose of the survey reports was to screen the various petrochemical processes into the "more" and "less - significantly polluting processes". Obviously, significance of pollution is a term which is difficult if not impossible to define because value judgements are involved. Recognizing this difficulty, a quantitative method for Significant Emission Index (SEI) was developed. This procedure is discussed and illustrated in Appendix II of this report. Each survey report includes the calculation of an SEI for the petrochemical that is the subject of the report. These SEI's have been incorporated into the Emission Summary Table that constitutes part of this Appendix (Table I). This table can be used as an aid when establishing priorities in the work required to set standards for emission controls on new stationary sources of air pollution in accordance with the terms of the Clean Air Amendments of 1970.

The completed survey reports constitute a preliminary data bank on each of the processes studied. In addition to the SEI calculation, each report includes a general introductory discussion of the process, a process description (including chemical reactions), a simplified process flow diagram, as well as heat and material balances. More pertinent to the air pollution study, each report lists and discusses the sources of air emissions (including odors and fugitive emissions) and the types of air pollution control equipment employed. In tabular form, each reports summarizes the emission data (amount, composition, temperature, and frequency); the sampling and analytical techniques; stack numbers and dimensions; and emission control device data (types, sizes, capital and operating costs, and efficiencies).

Calculation of efficiency on a pollution control device is not necessarily a simple and straight-forward procedure. Consequently, two rating techniques were developed for each type of device, as follows:

1. For flares, incinerators, and boilers a Completeness of Combustion Rating (CCR) and Significance of Emission Reduction Rating (SERR) were used.

2. For scrubbers and dust removal equipment, a Specific Pollutant Efficiency (SE) and a SERR were used.

The bases for these ratings and example calculations are included in Appendix III of this report.

II. In-Depth Studies

The original performance concept was to select a number of petrochemical processes as "significant polluters", on the basis of data contained in completed questionnaires. These processes were then to be studied "in-depth". However, the overall time schedule was such that the EPA requested an initial selection of three processes on the basis that they would probably turn out to be "significant polluters". The processes selected in this manner were:

1. The Furnace Process for producing Carbon Black.

2. The Sohio Process for producing Acrylonitrile.

3. The Oxychlorination Process for producing 1,2 Dichloroethane (Ethylene Dichloride) from Ethylene.

TABLE 1
EMISSIONS SUMMARY

	ESTIMATED (1) CURRENT AIR EMISSIONS, MM LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5)
Acetaldehyde via Ethylene	1.1	0	0	0	0	1.1	86
via Ethanol	0	0	0	0	27	27	27
Acetic Acid via Methanol	0	0	0.01	0	0	0.01	1
via Butane	40	0	0.04	0	14	54	3,215
via Acetaldehyde	6.1	0	0	0	1.3	7.4	490
Acetic Anhydride via Acetic Acid	3.1	0	0	0	5.5	8.6	253
Acrylonitrile (9)	183	0	5.5	0	196	385	15,000
Adipic Acid	0	0.2	29.6	0	0.14	30	1,190
Adiponitrile via Butadiene	11.2	4.7	50.5	0	0	66.4	3,200
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	156	8.1	6.9	21.6	3,870	4,060	17,544
Carbon Disulfide	0.15	0.3	0.1	4.5	0	5.1	120
Cyclohexanone	70	0	0	0	77.5	148	5,700
Dimethyl Terephthalate (+TPA)	91	1.4	0.1	1.0	53	146.5	7,460
Ethylene	15	0.2	0.2	2.0	0.2	17.6	1,240
Ethylene Dichloride via Oxychlorination	95.1	0.4	0	0	21.8	117.3	7,650
via Direct Chlorination	29	0	0	0	0	29	2,300
Ethylene Oxide	85.8	0	0.3	0.1	0	86.2	6,880
Formaldehyde via Silver Catalyst	23.8	0	0	0	107.2	131	1,955
via Iron Oxide Catalyst	25.7	0	0	0	24.9	50.6	2,070
Glycerol via Epichlorohydrin	16	0	0	0	0	16	1,280
Hydrogen Cyanide Direct Process	0.5	0	0.41	0	0	0.91	56
Isocyanates	1.3	0.8	0	0.02	86	88	231
Maleic Anhydride	34	0	0	0	260	294	2,950
Nylon 6	0	1.5	0	0	0	1.5	90
Nylon 6,6	0	5.5	0	0	0	5.5	330
Oxo Process	5.25	0.01	0.07	0	19.5	24.8	440
Phenol	24.3	0	0	0	0	24.3	1,940
Phthalic Anhydride via O-Xylene	0.1	5.1	0.3	2.6	43.6	51.7	422
via Naphthalene	0	1.9	0	0	45	47	160
High Density Polyethylene	79	2.3	0	0	0	81.3	6,400
Low Density Polyethylene	75	1.4	0	0	0	76.4	6,100
Polypropylene	37.5	0.1	0	0	0	37.6	2,950
Polystyrene	20	0.4	0	1.2	0	21.6	1,650
Polyvinyl Chloride	62	12	0	0	0	74	5,700
Styrene	4.3	0.07	0.14	0	0	4.5	355
Styrene-Butadiene Rubber	9.4	1.6	0	0.9	0	12	870
Vinyl Acetate via Acetylene	5.3	0	0	0	0	5.3	425
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	17.6	0.6	0	0	0	18.2	1,460
Totals	1,227.6	49.1	94.2	33.9	4,852.6	6,225.9 (7)	110,220 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons = 80, particulates = 60, NO_x = 40, SO_x = 20, and CO = 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) Emissions based on what is now an obsolete catalyst. See Report No. EPA-450/3-73-006 b for up-to-date information.

TABLE I
EMISSION SUMMARY

	ESTIMATED ADDITIONAL (2) AIR EMISSIONS IN 1980, 000 LBS./YEAR						
	Hydrocarbons (3)	Particulates (4)	Oxides of Nitrogen	Sulfur Oxides	Carbon Monoxide	Total	Total Weighted (5,6)
Acetaldehyde via Ethylene	1.2	0	0	0	0	1.2	96
via Ethanol	0	0	0	0	0	0	0
Acetic Acid via Methanol	0	0	0.04	0	0	0.04	2
via Butane	0	0	0	0	0	0	0
via Acetaldehyde	12.2	0	0	0	2.5	14.7	980
Acetic Anhydride via Acetic Acid	0.73	0	0	0	1.42	2.15	60
Acrylonitrile (9)	284	0	8.5	0	304	596	23,000
Adipic Acid	0	0.14	19.3	0	0.09	19.5	779
Adiponitrile via Butadiene	10.5	4.4	47.5	0	0	62.4	3,010
via Adipic Acid	0	0.5	0.04	0	0	0.54	30
Carbon Black	64	3.3	2.8	8.9	1,590	1,670	7,200
Carbon Disulfide	0.04	0.07	0.03	1.1	0	1.24	30
Cyclohexanone	77.2	0	0	0	85.1	162	6,260
Dimethyl Terephthalate (+TPA)	73.8	1.1	0.07	0.84	42.9	118.7	6,040
Ethylene	1.8	0.2	0.2	61.5	0.2	77	2,430
Ethylene Dichloride via Oxychlorination	110	0.5	0	0	25	136	8,800
via Direct Chlorination	34.2	0	0	0	0	34.2	2,740
Ethylene Oxide	32.8	0	0.15	0.05	0	33	2,650
Formaldehyde via Silver Catalyst	14.8	0	0	0	66.7	81.5	1,250
via Iron Oxide Catalyst	17.6	0	0	0	17.0	34.6	1,445
Glycerol via Epichlorohydrin	8.9	0	0	0	0	8.9	700
Hydrogen Cyanide Direct Process	0	0	0	0	0	0	0
Isocyanates	1.2	0.7	0	0.02	85	87	225
Maleic Anhydride	31	0	0	0	241	272	2,720
Nylon 6	0	3.2	0	0	0	3.2	194
Nylon 6,6	0	5.3	0	0	0	5.3	318
Oxo Process	3.86	0.01	0.05	0	14.3	18.2	325
Phenol	21.3	0	0	0	0	21.3	1,704
Phthalic Anhydride via O-Xylene	0.3	13.2	0.8	6.8	113	134	1,100
via Naphthalene	0	0	0	0	0	0	0
High Density Polyethylene	210	6.2	0	0	0	216	17,200
Low Density Polyethylene	262	5	0	0	0	267	21,300
Polypropylene	152	0.5	0	0	0	152.5	12,190
Polystyrene	20	0.34	0	1.13	0	21.47	1,640
Polyvinyl Chloride	53	10	0	0	0	63	4,840
Styrene	3.1	0.05	0.1	0	0	3.25	225
Styrene-Butadiene Rubber	1.85	0.31	0	0.18	0	2.34	170
Vinyl Acetate via Acetylene	4.5	0	0	0	0	4.5	360
via Ethylene	0	0	TR	0	0	TR	TR
Vinyl Chloride	26.3	0.9	0	0	0	27.2	2,170
Totals	1,547.2	55.9	79.5	80.5	2,588	4,351.9	134,213 (7)

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 40, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(9) See sheet 1 of 3.

TABLE I
EMISSIONS SUMMARY

	Emissions (2), MM Lbs./Year		Estimated Number of New Plants (1973 - 1980)	Total Estimated Capacity MM Lbs./Year	
	Total by 1980	Total Weighted (5) by 1980		Current	By 1980
Acetaldehyde via Ethylene	2.3	182	6	1,160	2,460
via Ethanol	27	27	0	960	960
Acetic Acid via Methanol	0.05	3	2	400	1,800
via Butane	54	3,215	0	1,020	500
via Acetaldehyde	22	1,470	8	875	2,015
Acetic Anhydride via Acetic Acid	10.8	313	8	1,705	2,100
Acrylonitrile (9)	980	38,000	5	1,165	3,700 (8)
Adipic Acid	50	1,970	-	1,430	2,200
Adiponitrile via Butadiene	128.8	6,210	4	435	845
via Adipic Acid	1.1	60	3	280	550
Carbon Black	5,730	24,740	13	3,000	5,000 (8)
Carbon Disulfide	6.3	150	2	871	1,100
Cyclohexanone	310	11,960	10	1,800	3,600
Dimethyl Terephthalate (+TPA)	265	13,500	8	2,865	5,900
Ethylene	94	3,670	21	22,295	40,000
Ethylene Dichloride via Oxychlorination	253	16,450	6	4,450	8,250 (8)
via Direct Chlorination	63	5,040	10	5,593	11,540
Ethylene Oxide	120	9,530	15	4,191	6,800 (8)
Formaldehyde via Silver Catalyst	212.5	3,205	40	5,914	9,000
via Iron Oxide Catalyst	85	3,515	12	1,729	3,520 (8)
Glycerol via Epichlorohydrin	25	2,000	1	245	380
Hydrogen Cyanide Direct Process	0.5 (10)	28 (10)	0	412	202
Isocyanates	175	456	10	1,088	2,120
Maleic Anhydride	566	5,670	6	359	720
Nylon 6	4.7	284	10	480	1,500
Nylon 6,6	10.8	650	10	1,523	3,000
Oxo Process	43	765	6	1,727	3,000
Phenol	46	3,640	11	2,363	4,200
Phthalic Anhydride via O-Xylene	186	1,522	6	720	1,800 (8)
via Naphthalene	47	160	0	603	528
High Density Polyethylene	297	23,600	31	2,315	8,500
Low Density Polyethylene	343	27,400	41	5,269	21,100
Polypropylene	190	15,140	32	1,160	5,800
Polystyrene	43	3,290	23	3,500	6,700
Polyvinyl Chloride	137	10,540	25	4,375	8,000
Styrene	7.4	610	9	5,953	10,000
Styrene-Butadiene Rubber	14	1,040	4	4,464	5,230
Vinyl Acetate via Acetylene	9.8	785	1	206	356
via Ethylene	TR	TR	4	1,280	2,200
Vinyl Chloride	45	3,630	10	5,400	13,000
Totals	10,605 (7)	244,420 (7)			

(1) In most instances numbers are based on less than 100% survey. All based on engineering judgement of best current control. Probably has up to 10% low bias.
(2) Assumes future plants will employ best current control techniques.
(3) Excludes methane, includes H_2S and all volatile organics.
(4) Includes non-volatile organics and inorganics.
(5) Weighting factors used are: hydrocarbons - 80, particulates - 60, NO_x - 40, SO_x - 20, and CO - 1.
(6) Referred to elsewhere in this study as "Significant Emission Index" or "SEI".
(7) Totals are not equal across and down due to rounding.
(8) By 1985.
(9) See sheet 1 of 3
(10) Due to anticipated future shut down of marginal plants.

In order to obtain data on these processes, the operators and/or licensors of each were approached directly by Air Products' personnel. This, of course, was a slow and tedious method of data collection because mass mailing techniques could not be used, nor could the request for data be identified as an "Official EPA Requirement". Yet, by the time that OMB approval was given for use of the Industry Questionnaire, a substantial volume of data pertaining to each process had already been received. The value of this procedure is indicated by the fact that first drafts of these three reports had already been submitted to the EPA, and reviewed by the Industry Advisory Committee, prior to the completion of many of the survey reports.

In addition, because of timing requirements, the EPA decided that three additional chemicals be "nominated" for in-depth study. These were phthalic anhydride, formaldehyde and ethylene oxide. Consequently, four additional in-depth studies were undertaken, as follows:

1. Air Oxidation of Ortho-Xylene to produce Phthalic Anhydride.

2. Air Oxidation of Methanol in a Methanol Rich Process to produce Formaldehyde over a Silver Catalyst. (Also, the subject of a survey report.)

3. Air Oxidation of Methanol in a Methanol-Lean Process to produce Formaldehyde over an Iron Oxide Catalyst.

4. Direct Oxidation of Ethylene to produce Ethylene Oxide.

The primary data source for these was the Industry Questionnaire, although SEI rankings had not been completed by the time the choices were made.

The Survey Reports, having now been completed are available, for use in the selection of additional processes for in-depth study.

INTRODUCTION TO APPENDIX II AND III

The following discussions describe techniques that were developed for the single purpose of providing a portion of the guidance required in the selection of processes for in-depth study. It is believed that the underlying concepts of these techniques are sound. However, use of them without substantial further refinement is discouraged because the data base for their specifics is not sufficiently accurate for wide application. The subjects covered in the Appendix II discussion are:

1. Prediction of numbers of new plants.

2. Prediction of emissions from the new plants on a weighted (significance) basis.

The subject covered in the Appendix III discussion is:

Calculation of pollution control device efficiency on a variety of bases, including a weighted (significance) basis.

It should be noted that the weighting factors used are arbitrary. Hence, if any reader of this report wishes to determine the effect of different weighing factors, the calculation technique permits changes in these, at the reader's discretion.

APPENDIX II

Number of New Plants*

Attached Table 1 illustrates the format for this calculation. Briefly, the procedure is as follows:

1. For each petrochemical that is to be evaluated, estimate what amount of today's production capacity is likely to be on-stream in 1980. This will be done by subtracting plants having marginal economics due either to their size or to the employment of an out-of-date process.

2. Estimate the 1980 demand for the chemical and assume a 1980 installed capacity that will be required in order to satisfy this demand.

3. Estimate the portion of the excess of the 1980 required capacity over today's remaining capacity that will be made up by installation of each process that is being evaluated.

4. Estimate an economic plant or unit size on the basis of today's technology.

5. Divide the total required new capacity for each process by the economic plant size to obtain the number of new units.

In order to illustrate the procedure, data have been incorporated into Table I, for the three processes for producing carbon black, namely the furnace process, the relatively non-polluting thermal process, and the non-growth channel process.

*The format is based on 1980, but any future year may be selected.

Table 1. Number of New Plants by 1980

Chemical	Process	Current Capacity	Marginal Capacity	Current Capacity on-stream in 1980	Demand 1980	Capacity 1980	Capacity to be Added	Economic Plant Size	Number of New Units
Carbon Black	Furnace	4,000	0	4,000	4,500	5,000	1,000	90	11 - 12
	Channel	100	0	100	100	100	0	30	0
	Thermal	200	0	200	400	500	300	150	2

Notes: 1. Capacity units all in MM lbs./year.

2. 1980 demand based on studies prepared for EPA by Processes Research, Inc. and MSA Research Corporation.

Increased Emissions (Weighted) by 1980

Attached Table 2 illustrates the format for this calculation. However, more important than format is a proposal for a weighting basis. There is a wide divergence of opinion on which pollutants are more noxious and even when agreement can be reached on an order of noxiousness, disagreements remain as to relative magnitudes for tolerance factors. In general pollutants from the petrochemical industry can be broken down into categories of hydrogen sulfide, hydrocarbons, particulates, carbon monoxide, and oxides of sulfur and nitrogen. Of course, two of these can be further broken down; hydrocarbons into paraffins, olefins, chlorinated hydrocarbons, nitrogen or sulfur bearing hydrocarbons, etc. and particulates into ash, catalyst, finely divided end products, etc. It was felt that no useful end is served by creating a large number of sub-groupings because it would merely compound the problem of assigning a weighting factor. Therefore, it was proposed to classify all pollutants into one of five of the six categories with hydrogen sulfide included with hydrocarbons.

There appears to be general agreement among the experts that carbon monoxide is the least noxious of the five and that NO_x is somewhat more noxious than SO_x. However, there are widely divergent opinions concerning hydrocarbons and particulates - probably due to the fact that these are both widely divergent categories. In recent years, at least two authors have attempted to assign tolerance factors to these five categories. Babcock (1), based his on the proposed 1969 California standards for one hour ambient air conditions with his own standard used for hydrocarbons.

On the other hand, Walther (2), based his ranking on both primary and secondary standards for a 24-hour period. Both authors found it necessary to extrapolate some of the basic standards to the chosen time period. Their rankings, on an effect factor basis with carbon monoxide arbitrarily used as a reference are as follows:

	Babcock	Walther	
		Primary	Secondary
Hydrocarbons	2.1	125	125
Particulates	107	21.5	37.3
NO_x	77.9	22.4	22.4
SO_x	28.1	15.3	21.5
CO	1	1	1

Recognizing that it is completely unscientific and potentially subject to substantial criticism it was proposed to take arithmetic averages of the above values and round them to the nearest multiple of ten to establish a rating basis as follows:

	Average	Rounded
Hydrocarbons	84.0	80
Particulates	55.3	60
NO_x	40.9	40
SO_x	21.6	20
CO	1	1

Table 2. Weighted Emission Rates

Chemical _____

Process _____

Increased Capacity _____

Pollutant	Emissions, Lbs./Lb.	Increased Emissions Lbs./Year	Weighting Factors	Weighted Emissions Lbs./Year
Hydrocarbons			80	
Particulates			60	
NO_x			40	
SO_x			20	
CO			1	
			Total	

Increased Emissions (Weighted) by 1980 (continued)

This ranking can be defended qualitatively, if not quantitatively for the following reasons:

1. The level of noxiousness follows the same sequence as is obtained using national air quality standards.

2. Approximately two orders of magnitude exist between top and bottom rankings.

3. Hydrocarbons should probably have a lower value than in the Walther analysis because such relatively non-noxious compounds as ethane and propane are included.

4. Hydrocarbons should probably have a higher value than in the Babcock analysis because such noxious (or posionous) substances as aromatics, chlorinated hydrocarbons, phenol, formaldehyde, and cyanides are included.

5. Particulates should probably have a higher value than in the Walther analysis because national air standards are based mostly on fly ash while emissions from the petrochemical industry are more noxious being such things as carbon black, phthalic anhydride, PVC dust, active catalysts, etc.

6. NO_x should probably have a higher value than in the Walther analysis because its role in oxidant synthesis has been neglected. This is demonstrated in Babcock's analysis.

Briefly, the procedure, using the recommended factors and Table 2, is as follows:

1. Determine the emission rate for each major pollutant category in terms of pounds of pollutant per pound of final product. (This determination was made on the basis of data reported on returned questionnaires in the Survey Reports).

2. Multiply these emission rates by the estimate of increased production capacity to be installed by 1980 (as calculated while determining the number of new plants), to determine the estimated pounds of new emissions of each pollutant.

3. Multiply the pounds of new emissions of each pollutant by its weighting factor to determine a weighted pounds of new emissions for each pollutant.

4. Total the weighted pounds of new emissions for all pollutants to obtain an estimate of the significance of emission from the process being evaluated. It was proposed that this total be named "Significant Emission Index" and abbreviated "SEI".

It should be pointed out that the concepts outlined above are not completely original and considerable credit should be given to Mr. L. B. Evans of the EPA for setting up the formats of these evaluating procedures.

Increased Emissions (Weighted) by 1980 (continued)

(1) Babcock, L. F., "A Combined Pollution Index for Measurement of Total Air Pollution," JAPCA, October, 1970; Vol. 20, No. 10; pp 653-659

(2) Walther, E. G., "A Rating of the Major Air Pollutants and Their Sources by Effect", JAPCA, May, 1972; Vol. 22, No. 5; pp 352-355

Appendix III
Efficiency of Pollution Control Devices

Incinerators and Flares

The burning process is unique among the various techniques for reducing air pollution in that it does not remove the noxious substance but changes it to a different and hopefully less noxious form. It can be, and usually is, a very efficient process when applied to hydrocarbons, because when burned completely the only products of combustion are carbon dioxide and water. However, if the combustion is incomplete a wide range of additional products such as cracked hydrocarbons, soot and carbon monoxide might be formed. The problem is further complicated if the hydrocarbon that is being burned is halogenated, contains sulfur or is mixed with hydrogen sulfide, because hydrogen chloride and/or sulfur oxides then become products of combustion. In addition, if nitrogen is present, either as air or nitrogenated hydrocarbons, oxides of nitrogen might be formed, depending upon flame temperature and residence time.

Consequently, the definition of efficiency of a burner, as a pollution control device, is difficult. The usual definition of percentage removal of the noxious substance in the feed to the device is inappropriate, because with this definition, a "smoky" flare would achieve the same nearly 100 percent rating, as a "smokeless" one because most of the feed hydrocarbon will have either cracked or burned in the flame. On the other hand, any system that rates efficiency by considering only the total quantity of pollutant in both the feed to and the effluent from the device would be meaningless. For example, the complete combustion of one pound of hydrogen sulfide results in the production of nearly two pounds of sulfur dioxide, or the incomplete combustion of one pound of ethane could result in the production of nearly two pounds of carbon monoxide.

For these reasons, it was proposed that two separate efficiency rating be applied to incineration devices. The first of these is a "Completeness of Combustion Rating" and the other is a "Significance of Emission Reduction Rating", as follows:

1. Completeness of Combustion Rating (CCR)

This rating is based on oxygen rather than on pollutants and is the pounds of oxygen that react with the pollutants in the feed to the device, divided by the theoretical maximum number of pounds that would react: Thus a smokeless flare would receive a 100 percent rating while a smoky one would be rated somewhat less, depending upon how incomplete the combustion.

In utilizing this rating, it is clear that carbon dioxide and water are the products of complete combustion of hydrocarbons. However, some question could occur as to the theoretical completion of combustion when burning materials other than hydrocarbons. It was recommended that the formation of HX be considered complete combustion of halogenated hydrocarbons since the oxidation most typically does not change the valence of the halogen. On the other hand, since some incinerators will be catalytic in nature it was recommended that sulfur trioxide be considered as complete oxidation of sulfur bearing compounds.

Efficiency of Pollution Control Devices

1. Completeness of Combustion Rating (CCR) (continued)

Nitrogen is more complex, because of the equilibria that exist between oxygen, nitrogen, nitric oxide, nitrogen dioxide and the various nitrogen radicals such as nitrile. In fact, many scientists continue to dispute the role of fuel nitrogen versus ambient nitrogen in the production of NO_x. In order to make the CCR a meaningful rating for the incineration of nitrogenous wastes it was recommended that complete combustion be defined as the production of N_2, thus assuming that all NO_x formed comes from the air rather than the fuel, and that no oxygen is consumed by the nitrogen in the waste material. Hence, the CCR becomes a measure of how completely the hydrocarbon content is burned, while any NO_x produced (regardless of its source) will be rated by the SERR as described below.

2. Significance of Emission Reduction Rating (SERR)

This rating is based primarily on the weighting factors that were proposed above. All air pollutants in the feed to the device and all in the effluents from the device are multiplied by the appropriate factor. The total weighted pollutants in and out are then used in the conventional manner of calculating efficiency of pollutant removal, that is pollutants in minus pollutants out, divided by pollutants in, gives the efficiency of removal on a significance of emission basis.

Several examples will serve to illustrate these rating factors. as follows:

Example 1 - One hundred pounds of ethylene per unit time is burned in a flare, in accordance with the following reaction:

$$3C_2H_4 + 7\,O_2 \longrightarrow C + 2\,CO + 3\,CO_2 + 6\,H_2O$$

Thus, 14.2 lbs. of particulate carbon and 66.5 lbs. of carbon monoxide are emitted, and 265 lbs. of oxygen are consumed.

Theoretical complete combustion would consume 342 lbs. of oxygen in accordance with the following reaction:

$$C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$$

Thus, this device would have a CCR of 265/342 or 77.5%

Assuming that one pound of nitric oxide is formed in the reaction as a result of the air used for combustion (this is about equivalent to 100 ppm), a SERR can also be calculated. It should be noted that the formation of this NO is not considered in calculating a CCR because it came from nitrogen in the air rather than nitrogen in the pollutant being incinerated. The calculation follows:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

Pollutant	Weighting Factor	Pounds in		Pounds out	
		Actual	Weighted	Actual	Weighted
Hydrocarbons	80	100	8000	0	
Particulates	60	0		14.2	852
NO_x	40	0		1	40
SO_x	20	0		0	
CO	1	0		66.5	66.5
Total			8000		958.5

$$SERR = \frac{8000 - 958.5}{8000} \times 100 = 88\%$$

Example 2 - The same as Example 1, except the hydrocarbons are burned to completion. Then,

$$CCR = \frac{342}{342} \times 100 = 100\%$$

and

$$SERR = \frac{8000 - 40}{8000} = 99.5\%$$

Example 3 - One hundred pounds per unit time of methyl chloride is incinerated, in accordance with the following reaction.

$$2\ CH_3Cl + 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O + 2\ HCl$$

This is complete combustion, by definition, therefore, the CCR is 100%. However, (assuming no oxides of nitrogen are formed), the SERR is less than 100% because 72.5 lbs. of HCl are formed. Hence, considering HCl as an aerosol or particulate;

$$SERR = \frac{100 \times 80 - 72.5 \times 60}{100 \times 80} \times 100 = 45.5\%$$

The conclusion from this final example, of course, is that it is an excellent combustion device but a very poor pollution control device, unless it is followed by an efficient scrubber for HCl removal.

Example 4 - The stacks of two hydrogen cyanide incinerators, each burning 100 pounds per unit time of HCN are sampled. Neither has any carbon monoxide or particulate in the effluent. However, the first is producing one pound of NO_x and the second is producing ten pounds of NO_x in the same unit time. The assumed reactions are:

Efficiency of Pollution Control Devices

2. Significance of Emission Reduction Rating (SERR) (continued)

$$4\ HCN + 5\ O_2 \longrightarrow 2\ H_2O + 4\ CO_2 + 2\ N_2$$

$$N_2\ (\text{atmospheric}) + XO_2 \longrightarrow 2\ NO_x$$

Thus, $CCR_1 = 100\%$ and $CCR_2 = 100\%$ both by definition.

However, $SERR_1 = \frac{100 \times 80 - 1 \times 40}{100 \times 80} \times 100 = 99.5\%$

and $SERR_2 = \frac{100 \times 80 - 10 \times 40}{100 \times 80} \times 100 = 95\%$

Obviously, if either of these were "smoky" then both the CCR and the SERR would be lower, as in Example 1.

Other Pollution Control Devices

Most pollution control devices, such as bag filters, electrostatic precipitators and scrubbers are designed to physically remove one or more noxious substances from the stream being vented. Typically, the efficiency of these devices is rated relative only to the substance which they are designed to remove and for this reason could be misleading. For example:

1. The electrostatic precipitator on a power house stack might be 99% efficient relative to particulates, but will remove little or none of the SO_x and NO_x which are usually present.

2. A bag filter on a carbon black plant will remove 99 + % of the particulate but will remove none of the CO and only relatively small amounts of the compounds of sulfur that are present.

3. A water scrubber on a vinyl chloride monomer plant will remove all of the hydrogen chloride but only relatively small amounts of the chlorinated hydrocarbons present.

4. An organic liquid scrubber on an ethylene dichloride plant will remove nearly all of the EDC but will introduce another pollutant into the air due to its own vapor pressure.

For these reasons, it was suggested again that two efficiency ratings be applied. However, in this case, the first is merely a specific efficiency as is typically reported, i.e., "specific to the pollutant (or pollutants) for which it was designed", thus:

$$SE = \frac{\text{specific pollutant in} - \text{specific pollutant out}}{\text{specific pollutant in}} \times 100$$

The second rating proposed is an SERR, defined exactly as in the case of incinerators.

Two examples will illustrate these ratings.

Efficiency of Pollution Control Devices

Other Pollution Control Devices (continued)

Example 1 - Assume that a catalytic cracker regenerator effluent contains 100 pounds of catalyst dust, 200 lbs. of carbon monoxide and 10 pounds of sulfur oxides per unit time. It is passed through a cyclone separator where 95 pounds of catalyst are removed. Therefore,

$$SE = \frac{100 - 5}{100} \times 100 = 95\%$$

$$\text{and } SERR = \frac{(100 \times 60 + 10 \times 20 + 200 \times 1) - (5 \times 60 + 10 \times 20 + 200 \times 1)}{(100 \times 60 + 10 \times 20 + 200 \times 1)} \times 100$$

$$= \frac{6400 - 700}{6400} \times 100 = 89\%$$

Example 2 - Assume that an organic liquid scrubber is used to wash a stream containing 50 pounds of SO_2 per unit time. All but one pound of the SO_2 is removed but two pounds of the hydrocarbon evaporate into the vented stream. Then

$$SE = \frac{50 - 1}{50} \times 100 = 98\%$$

$$\text{and } SERR = \frac{(50 \times 20) - (1 \times 20 + 2 \times 80)}{(50 \times 20)} \times 100$$

$$= \frac{1000 - 180}{1000} \times 100 = 82\%$$